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Distribution, origins and
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DISTRIBUTION, ORIGINS AND BEHAVIOUR OF LOCAL GROUNDWATERS CONTAINING ELEVATED CONCENTRATIONS OF CHLORIDES

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Prepared For
Ontario Ministry of the Environment

AUGUST 1988

By

Principal Investigator: Dr. K.W.F. Howard
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Scarborough Campus
UNIVERSITY OF TORONTO

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GROUNDWATER RESEARCH GROUP
SCARBOROUGH CAMPUS
UNIVERSITY OF TORONTO

Project No. 145

Distribution, Origins and Behaviour of Local Groundwaters Containing Elevated Concentrations of Chlorides

Final
Report to

The Ontario Ministry of The Environment

August, 1988

Principal Investigator: Dr. K.W.F. Howard
Research Associate: P. E. Orsini
Project Technician: M. Hughes
Laboratory Technician: L. Popiel

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This report is issued to describe an environmentally orientated research project conducted in Ontario and supported by grant by the Ministry of the Environment.

K.W.F. Howard

August, 1988

1. INTRODUCTION

1.1 Reporting

The three year research project commenced in October, 1984 following project confirmation and receipt of an administrative digest in August of the same year. The first progress report was submitted on March 26th, 1985 and included work completed during the first 6 months of the study. A second progress report was submitted on June 16th, 1986, and presented a summary of the progress achieved during the subsequent 15 month period. In addition, research papers were presented at Ministry of the Environment Technology Transfer Conferences in 1985 and 1986. This document represents the final project report.

1.2 Background to the Investigation

Shallow aquifer systems in surficial Quaternary sediments are a primary groundwater resource throughout much of south-central Ontario. Due to the geometrical complexity of these sediments and their highly variable hydraulic characteristics, these aquifers are extremely susceptible to groundwater contamination with many groundwaters throughout the area showing chloride concentrations considerably in excess of the anticipated background level. In many cases, (e.g. Sibul et al., 1977), elevated concentrations of chloride and associated major ions, result in total dissolved solids concentrations exceeding the maximum desirable level of 500 mg/L.

Sources of contamination responsible for chloride enrichment are numerous, particularly in Metropolitan Toronto and environs where the diversity of urban, agricultural and industrial activities provide a considerable range of potential pollutants. Possible unnatural sources of chloride include point sources such as landfilled municipal and industrial wastes and non-point sources such as road de-icing chemicals, certain fertilizers and the chemical products of urban development. To these must be added natural non-point sources of chloride such as saline formation waters commonly associated with bedrock aquitards. Point sources of contamination receive most media/research attention but tend to cause only localized contamination. Non-point sources on the other hand, often result in the long-term accumulation of contaminants in the shallow sub-surface which when released to aquifer systems can cause rapid and widespread degradation of water quality.

The value of chloride as an indicator of groundwater contamination in shallow aquifers is unquestionable. The ion is easily and routinely determined using standard analytical procedures. It is also, by nature, extremely conservative, being virtually unaffected by biological and chemical processes (for example, ion-exchange, oxidation/reduction, precipitation etc.) that retard the movement of all other routinely determined major ion parameters. The major difficulty lies in recognizing situations where elevated chloride concentrations are attributable to unnatural (non-aquifer) sources and subsequently differentiating between the various possible contaminant origins.

Traditionally, attempts to identify sources of groundwater contamination have focused on the detection of specific toxic materials believed to be present in the alleged contaminant source. Unfortunately, these toxic materials tend to occur in concentrations close to detection limits and are extremely difficult and expensive to determine with any precision. Furthermore, some of the toxic materials can occur naturally in sub-surface waters, thus giving rise to potentially misleading data. Consequently this approach is often inconclusive and rarely satisfactory.

Contamination problems are not restricted to source identification. In recent years contaminant studies have tended to focus on leachate migration from landfills. By comparison, the potential hazards associated with non-point sources have received little attention and the mechanisms of sub-surface accumulation and transport of contaminants derived in this way are not well understood. Road de-icing chemicals are a good example. In the Don River watershed of Metropolitan Toronto, studies by Paine (1979) have indicated that as little as 50% of chloride applied as road salt is being removed from the catchment by stream flow. This implies that the considerable excess, amounting to as much as 25,000 tonnes of chloride is accumulating annually in the shallow sub-surface of the watershed. The importance of the issue cannot be over emphasized. In its 1979 report, the WHO Working Group drew attention to studies that associated the intake of sodium, the counter-ion to chloride in most de-icing salts, with hypernatraemia and "sudden infant death". It is also recognized that sodium may have serious adverse physiological effects on individuals with cardiac, renal and circulatory problems (Moses, 1980) and, together with chloride (Morris and Kurtz, 1984), the ion has been linked with hypertension affecting over two million Canadians. It has been suggested by the American Heart Association that the recommended maximum concentration of sodium in drinking water be set at 22 mg/L, a level exceeded in 141 of 182 groundwater samples collected from roadside wells in York Region of southern Ontario by Joy (1979).

1.3 Project Objectives

The study has utilized major ion, minor ion, and trace metal hydrochemistry to address three primary objectives:

1) To determine the natural background levels of major ions (Ca, Na, Mg, K, HCO_3, Cl, NO_3, and SO_4), minor ions (I, F, Br) and trace metals (Mn, P, Al, Fe, Ba, B, Cd, Cr, Co, Se, Sb, As, V, Zn) in uncontaminated, naturally evolving groundwaters in shallow, surficial sediments. Until this is known, it would be extremely difficult to recognize chemical anomalies that are conclusively indicative of groundwater contamination.

2) To characterize potential contaminant sources by means of major ion, minor ion and trace metal parameters. This screening process allows recognition of constituents which may prove diagnostic indicators of contaminant source.

3) To confirm that non-point source contaminants are accumulating in the shallow sub-surface, and to develop, through a knowledge of their sub-surface chemical character, a convenient and definitive hydrochemical method of identifying the contaminant origins.

Throughout the study, emphasis has been placed on non-point contaminant sources that include fertilizers, road de-icing chemicals and bedrock waters. Point source contamination from landfill sites and sundry agricultural sources have also been considered to a lesser extent.

1.4 Report Format

The first three sections of the report provide background information for the hydrochemical study. Following this current introductory section (Section 1), Section 2 describes the Pleistocene geology, land use and rationale for choosing the study areas, and Section 3 discusses the two major hydrochemical studies previously undertaken in the study areas as well as previous research on non-point contamination of aquifers and the unsaturated zone. The rationale and field methods of the hydrochemical study are presented in Section 4. This is followed with a discussion of results in Sections 5 and 6. The conclusions and recommendations are contained in Section 7.

Supplementary information is presented as Appendices to the main body of the report. A summary of the analytical techniques used in this study is given in Appendix I. Analytical results of groundwaters, non-point source contaminants, and interstitial waters are given in Appendices II, III, and IV while the results of sediment analyses are provided in Appendix V. Distribution maps of major, minor, and trace constituents are provided in Appendix VI.

2. STUDY AREAS AND GEOLOGICAL HISTORY

2.1 Introduction

The study was conducted principally in two areas - Metropolitan Toronto and the Duffins Creek-Rouge River drainage basin. A third minor area, east of Brantford was chosen for one sample site due to difficulties in sampling in the Duffins Creek-Rouge River basin. The geologic and land use history of the three study areas are discussed below.

2.2 Study Areas

2.2.1 Duffins Creek-Rouge River Drainage Basins

The Duffins Creek-Rouge River drainage basins can be considered the primary study area, as it was used to determine the background chemistry of the naturally evolving groundwaters. This basin was ideally suited since it had been the subject of two previous hydrochemical studies (Sibul, 1979; Beck, 1985). As a result, something was known about the evolving major ion chemical character of the waters. Geological investigations of the basins have also been completed by Karrow (1967) and Westgate (1983).

Due to its rural setting and predominantly, though not exclusively agricultural land use, the basin proved particularly suitable for investigating contamination by organic and inorganic fertilizers and road de-icing chemicals. The basins are located to the north and east of Metropolitan Toronto as shown in Figure 2.1.

2.2.2 East Metropolitan Toronto

The eastern part of Metropolitan Toronto (Figure 2.2) was chosen to investigate non-point contamination from urban sources and road de-icing chemicals. Sediment augering and interstitial pore water sampling was conducted along a 10 km length of the Don Valley Parkway from Bloor Avenue in the south, to Eglington Avenue in the north. Comprehensive sampling of spring waters was also undertaken along the Scarborough Bluffs adjacent to lake Ontario.

2.2.3 Brantford

Because of the difficulty in obtaining access to suitable agricultural land in the Duffins Creek-Rouge River drainage basins, part of the study was carried out on agricultural land located 2.5km east of the city of Brantford (Figure 2.3). The Brantford site was chosen because access was easy and the agricultural practices of the farmers at this location were well known by the investigators. The area is part of the Erie drainage system and belongs to the Grand River drainage basin.

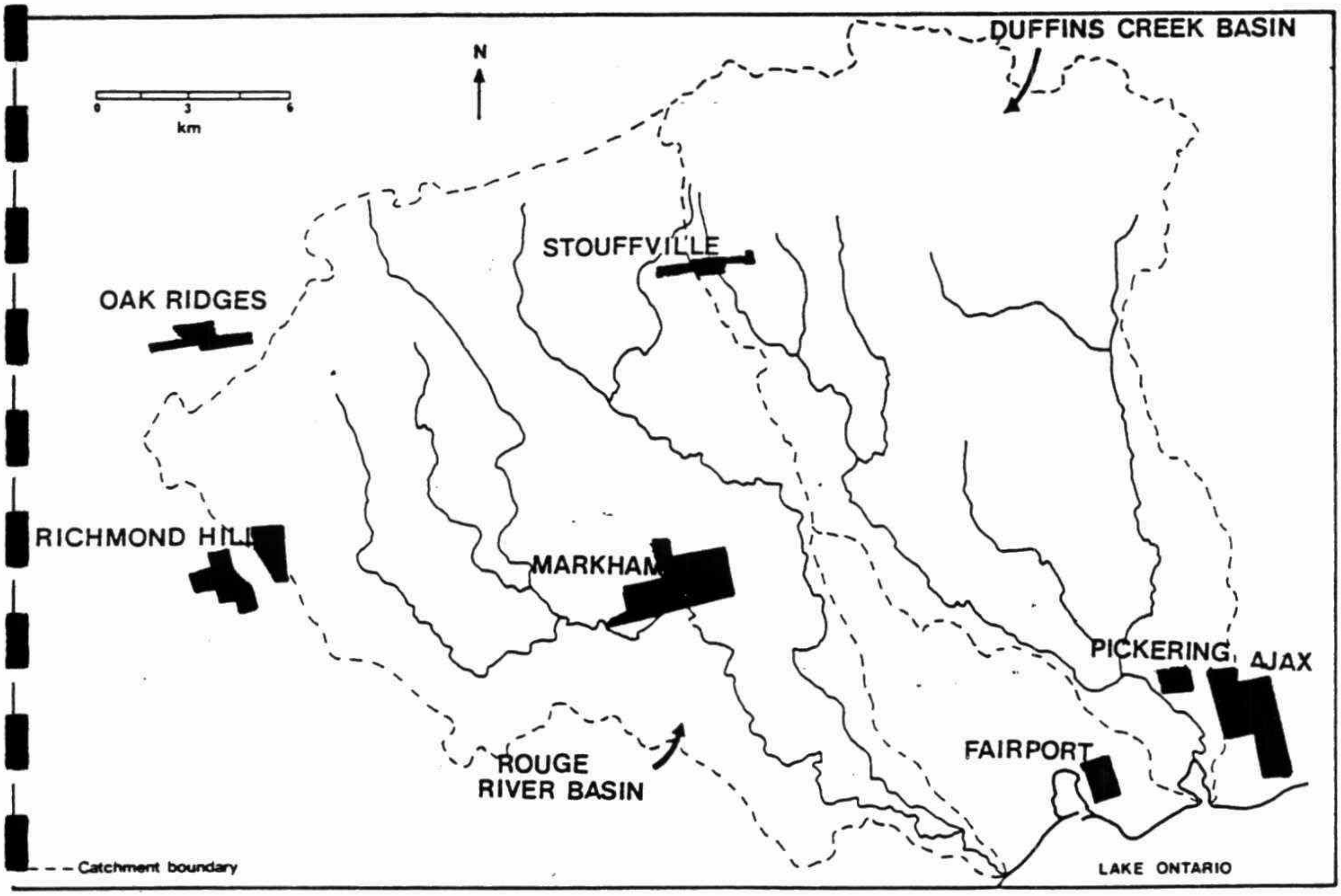
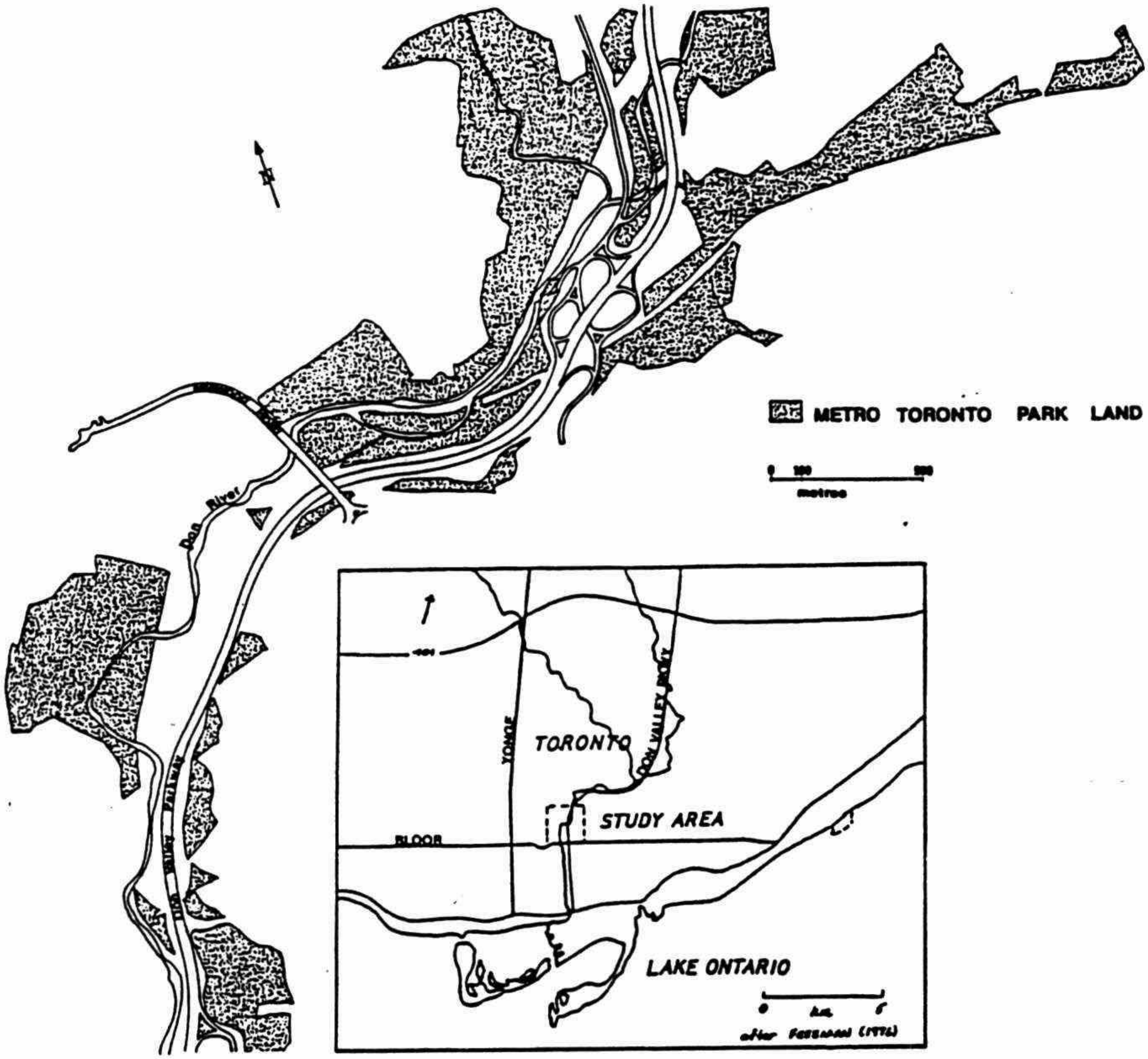


FIGURE 2.1 Map showing the location of the Duffins Creek-Rouge River basins Study area (Howard and Beck, 1986)



after Freeman (1976)

FIGURE 2.2 Location map showing east Metropolitan Toronto Study area

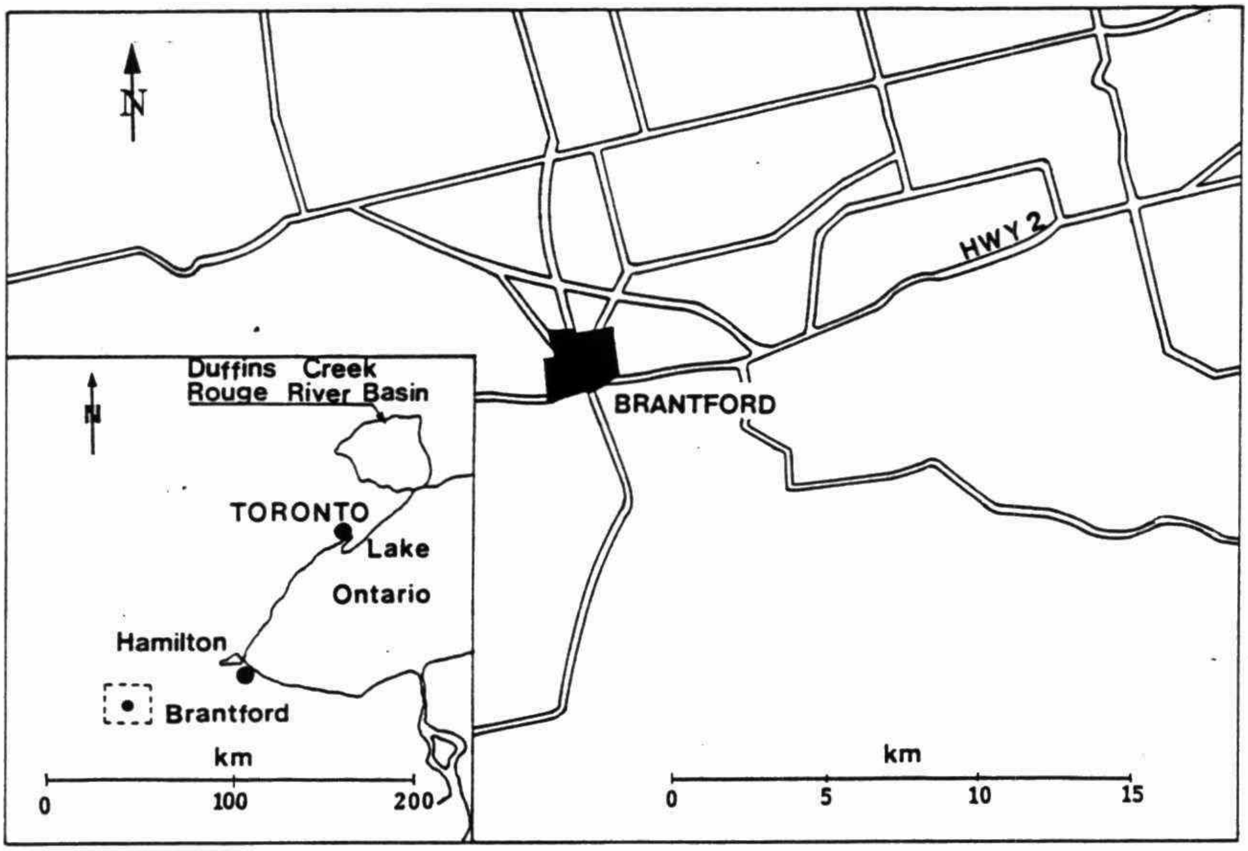


FIGURE 2.3 Location map showing Brantford area

2.3 Land Use

2.3.1 Duffins Creek-Rouge River Basins

In the Duffins Creek-Rouge River Basins, land use is predominantly agricultural or abandoned agricultural (MacLaren, 1979). The transition to residential and industrial is one of the most significant factors affecting groundwater supplies and usage. A study completed in 1979 by MacLaren Consultants indicated that industrial and residential land use in the basins had increased in the range 4 to 9 per cent. Present urbanization centres include Pickering and Ajax in the Duffins Creek basin, and the northern and eastern edges of Metropolitan Toronto, Richmond Hill, Markham and Unionville in the Rouge River basin (Figure 2.4).

2.3.2 East Metropolitan Toronto

The East Metropolitan Toronto site contains the Don River which drains into Lake Ontario. Land use in this portion of the Don Valley is densely urbanized commercial and residential (approximately 45%) with about 13 % of the land used for industrial purposes (MacLaren, 1979). As shown in Figure 2.5, a sewage treatment plant, a snow dump site, and a small industrial area are located within the confines of the study area. In addition to this, the Don Valley Parkway, a major north-south urban highway parallels the Don River and is noted for its high traffic volume.

The Scarborough Bluffs also represent a heavily urbanized area, but are predominantly residential with little industrial activity. While parts of the Bluffs are noted for their picturesque parkland, in most cases the urban development extends to the very edge of the bluff top.

2.3.3 Brantford

Land use in the area east of Brantford is almost exclusively agricultural with pockets of residential areas (Figure 2.6) located near railways and along major highways. Industrial encroachment from Ancaster and Hamilton has only begun within the last five years.

2.4 Study Area Geology

The geology of the Duffins Creek-Rouge River basins and the Toronto area consists of Paleozoic bedrock overlain by Pleistocene glacial sediments.

Throughout the region, the bedrock comprises Cambrian-Ordovician marine sediments (shales and limestones) belonging to the Whitby and Georgian Bay Formations. The Whitby Formation, which disconformably overlies the Lindsay Formation, was deposited in a shallow marine environment and varies in thickness from 79.3 to 88.4 m. It is overlain by grey shales and interbedded limestones of the Georgian Bay Formation which was deposited in a shallow water marine environment. Thicknesses range from 183m to 250 m (Beck, 1985).

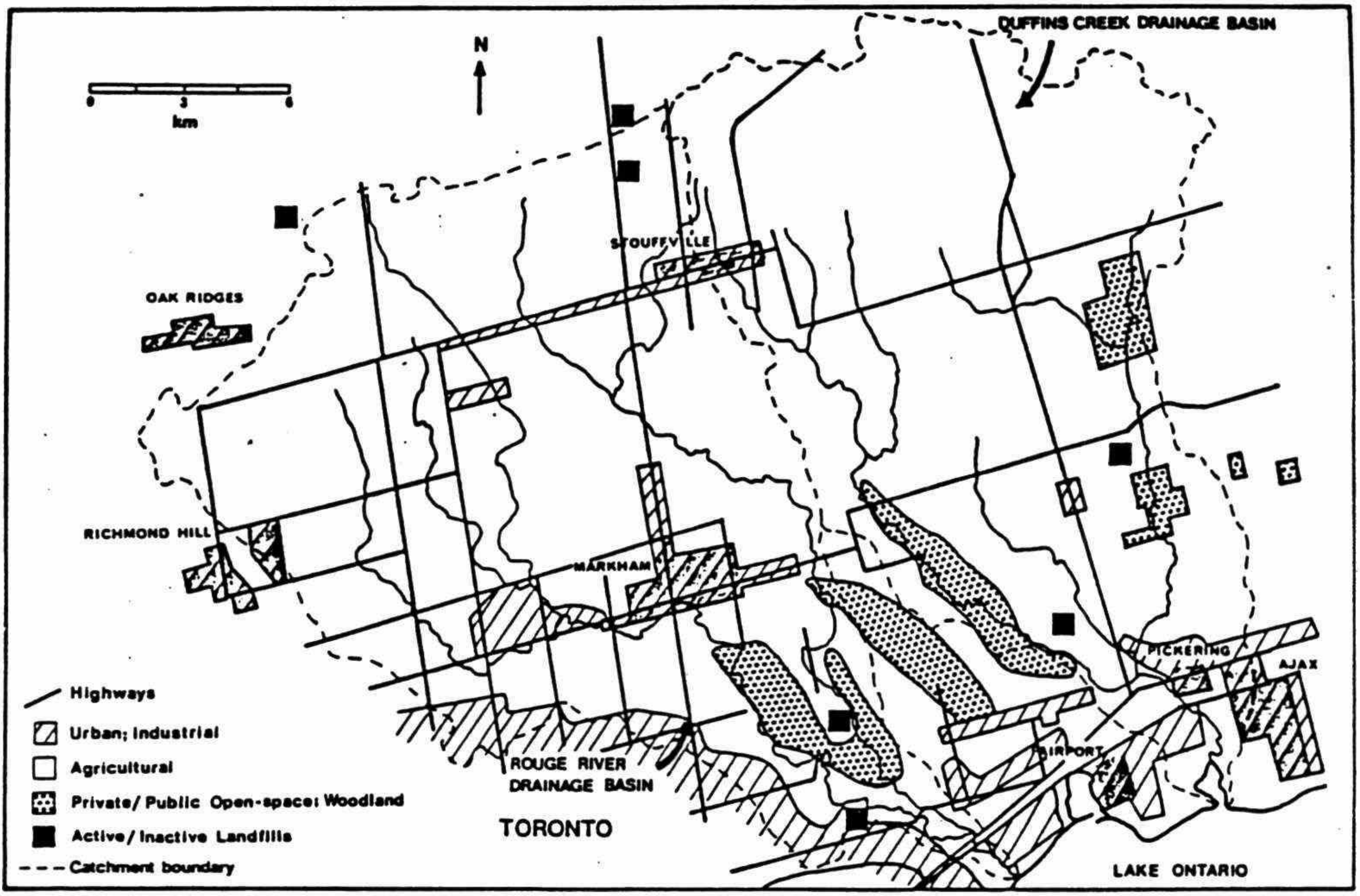


Figure 2.4 Land use map for Duffins Creek-Rouge River basins (Howard and Beck, 1986)

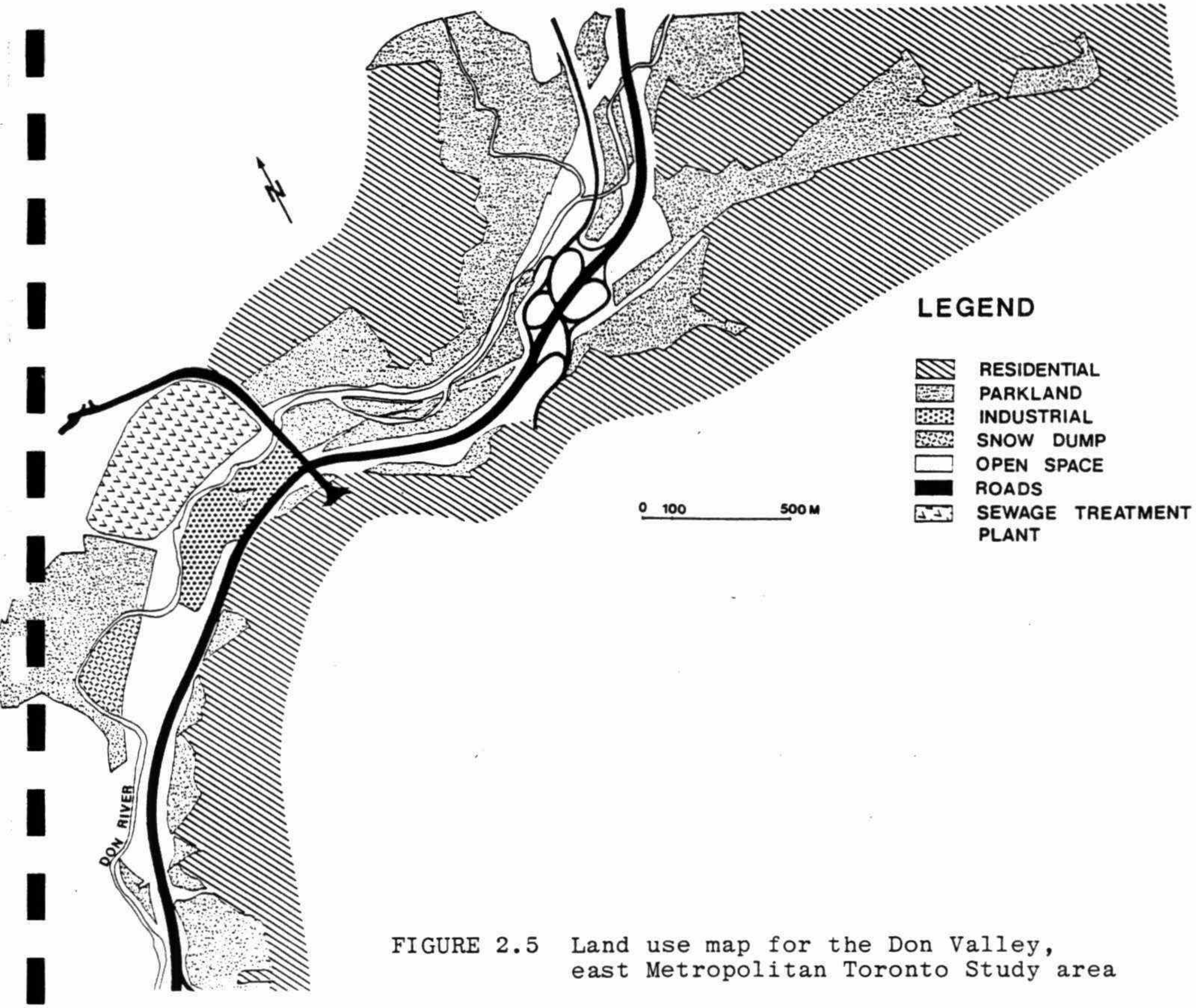


FIGURE 2.5 Land use map for the Don Valley, east Metropolitan Toronto Study area

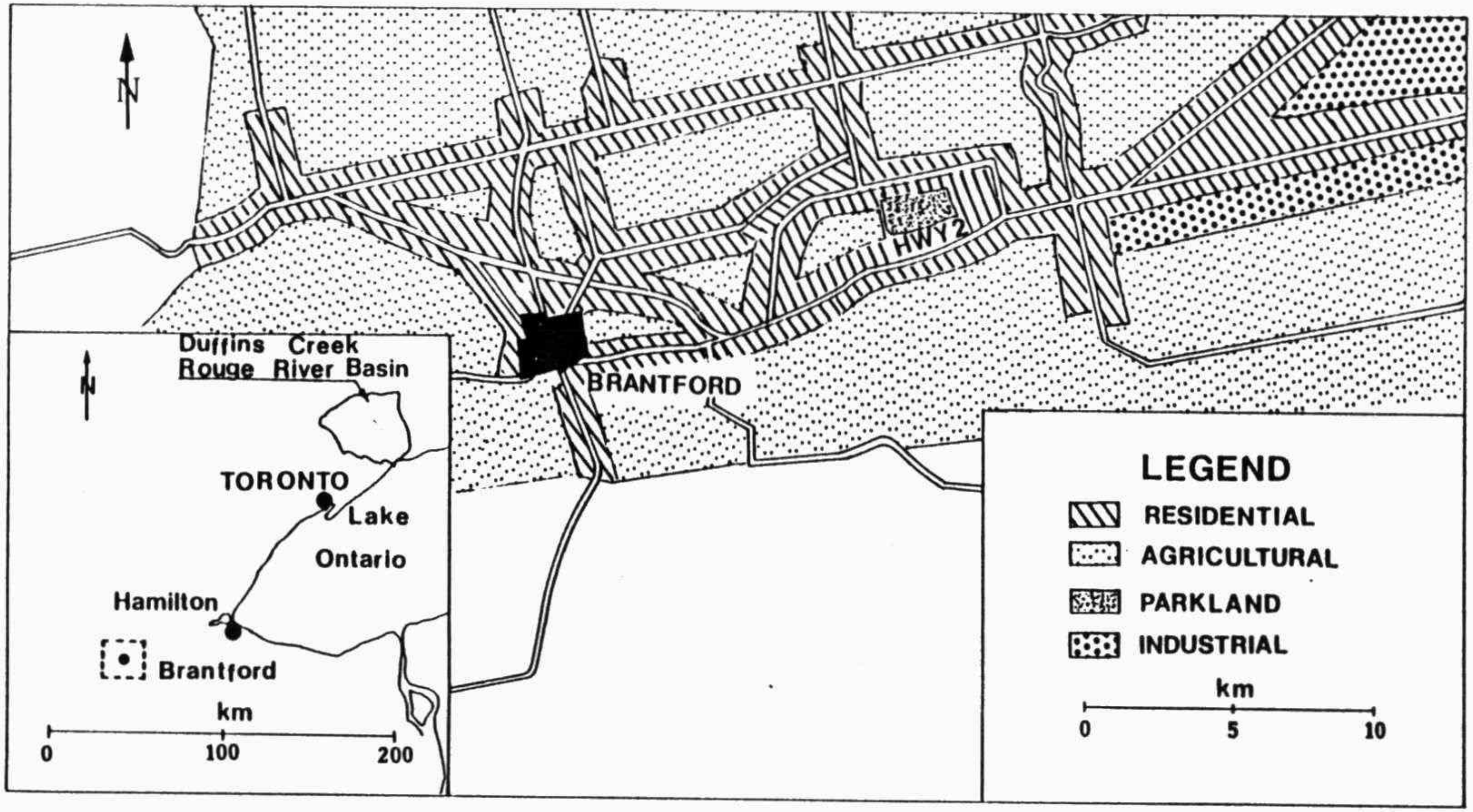


FIGURE 2.6 Land use map for the Brantford area

Most of the important aquifers are developed within the overlying Pleistocene sediments. Table 2.1 outlines the Pleistocene stratigraphy for the Duffins Creek-Rouge River basin and Toronto area based on the work of Karrow (1967) and Eyles (1982), and Eyles and Eyles (1983).

Table 2.1 Geological Formations and Events*

Stage	Formation or Event	Lithology
Recent	Lake Ontario beaches	Beach, sand, gravel
	Alluvium	Clay,silt,sand,gravel
	Swamp,bog deposits	Marl,muck,peat
	Stream terrace deposits	Clay,sand,gravel
Late Wisconsinan	Lake Iroquois	Clay,sand,gravel
	Early peripheral lakes	Clay,sand
	Halton Till	Silty sand diamict
	Lake,stream deposits	Varved clay,sand
	Meadowcliffe	Silty clay diamict
	Lake,stream deposits	Varved clay,sand
	Seminary	Clayey sand diamict
Middle Wisconsinan	Thorncliffe Formation	Varved clay,sand
Early Wisconsinan	Sunnybrook Diamict	Silty,clay diamict
	Scarborough Formation	Clay,silt,sand,wood
Sangamonian	Don Formation	Clay,sand,wood
Illinoian	York Till	Clayey,sand diamict

* after Karrow (1967), Beck (1985)

The Pleistocene sediments are the product of two major glacial episodes. The older glacial episode is dated as Illinoian. Evidence of this glaciation comes from the York Till which is believed to have been deposited during Illinoian age by ice moving from the northeast. Following the Illinoian glacial episode, the Don Formation (a stratified clay and sand) was deposited during the Sangamonian interglacial period approximately 125,000 years B.P. (Beck, 1985).

The second glacial episode known as the Wisconsinan began at least 60,000 years B.P.. The beginning of the glacial episode is evidenced by the lower lacustrine silt and clay unit of the Scarborough Formation which is believed to represent a prodelta deposit. This unit grades upward into a fine to coarse grained sand with organic rich laminae and well developed planar and cross stratification. These Scarborough Formation sands are thought to represent a prograding delta deposit.

The Scarborough Formation is overlain by the Sunnybrook diamict which is a poorly sorted silty clay with pebble-sized clasts. In the basal portion of the Sunnybrook diamict the clasts are boulder-sized and are more abundant. Initially, the Sunnybrook was classified as a sub-glacial ice-laid deposit, i.e. a "till". However, based on the sedimentological and micropalaeontological characteristics of the Sunnybrook Formation, Eyles and Eyles (1983) have proposed a glaciolacustrine origin for this unit. Eyles and Eyles have suggested that the Sunnybrook is a diamict deposited below floating ice (glacier ice ramps, shelves, bergs, lake ice) in a large lacustrine basin which experienced a large influx of fine-grained suspended sediment. This interpretation was also proposed for two other "tills" in the Quaternary succession, the Seminary and Meadowcliffe. The presence of undiversified lacustrine ostracode fauna (for example, *Candona cf. C. subtriangulata*) which are in-situ also suggests that the depositional environment was a large, deep and cold lake (Westgate et al., 1987 in press).

Overlying the Sunnybrook diamict is the Thorncliffe Formation which is comprised of fine grained sands, silts and clays. Eyles and Eyles (1983) have suggested that the Thorncliffe represents basinward delta growth over the Sunnybrook diamict and interbedded with the Seminary and Meadowcliffe diamicts. While Karrow (1967), asserts that the Seminary and Meadowcliffe diamicts represent tills from minor glacial ice advances during the Middle Wisconsinan, the Eyles group believes that they more likely represent glaciolacustrine sediments, similar to the Sunnybrook diamict. The Seminary diamict ranges in composition from silty clay to stratified sand while the thicker Meadowcliffe unit consists of silty clays. These diamicts are overlain by the Halton Till which is an extremely variable silty sand.

During the later part of the Wisconsinan glaciation, the ice sheet split into two lobes. One lobe retreated southward towards Lake Ontario depositing thick sequences of sands and gravels known as the Oak Ridges Moraine. This moraine extends 160 km from King City along the northern part of the Duffins Creek-Rouge River drainage basins study area to Rice Lake. The northern lobe retreated into the Lake Simcoe area (Sibul et al., 1977).

As the ice sheet gradually melted, stratified silts and clays were deposited in the centre of the basin where extensive shallow lakes formed. These lacustrine deposits are sometimes associated with gravel beds 1-2m thick (Beck, 1985; Sibul et al. 1977).

3. PREVIOUS HYDROCHEMICAL INVESTIGATIONS

3.1 Introduction

Although groundwater hydrochemistry is a relatively new area of hydrogeological research, two hydrochemical studies (Sibul et al., 1977; and Beck, 1985) have been conducted previously in the project area. In addition, there have been numerous studies by other investigators that have a direct relevance to the current research problem. All this material deserves careful attention. Section 3.2 reviews the work of Sibul et al. (1977) and Beck (1985) conducted in the Duffins Creek- Rouge River drainage basins. The subsequent section (3.3) summarizes previous hydrochemical investigations of groundwater contamination resulting from such sources as road de-icing chemicals, inorganic fertilizers, urban development, and landfill sites.

3.2 Hydrochemical Investigations of Groundwater in the Duffins Creek - Rouge River Basins.

As indicated in Section 2, an important consideration in the selection of the the Duffins Creek-Rouge River basin study area was the availability of baseline studies by previous researchers. In the first study, Sibul et al. (1977) defined 14 aquifer systems in the overburden sediments of the basins, primarily on the basis of borehole records. This study also showed that 30% of groundwaters in the basin contained total dissolved solids (TDS) in excess of the 500 mg/L limit as recommended by the Ministry of the Environment guidelines (MOE, 1984). The authors suggested that the high concentrations of total dissolved solids were the result of contamination, and speculated that a wide range of pollutants may have been responsible. They did recognise that most of the overburden groundwaters could be classified as calcium-bicarbonate waters (Figure 3.1) and contrasted in character to the deeper bedrock groundwaters of the area which were described as either sodium bicarbonate or salty and/or sulphurous in type. With their limited chemical data, the authors of the study were unable to provide a more rigorous hydrochemical interpretation.

Detailed follow-up work by Beck (1985) was able to determine the behaviour of the aquifer systems in a regional context. Using major and minor ion hydrochemical parameters, Beck showed that the aquifer systems previously defined by Sibul et al. (1977) did not behave as individual discrete aquifer units but were part of a regional composite groundwater flow system. He showed that the individual aquifer systems could not be distinguished on the basis of their hydrochemical character, but that the groundwaters displayed regional hydrochemical variations that were the product of natural chemical evolution of the groundwaters on a basin wide scale.

Beck's interpretation was based on a chemical classification scheme shown in Table 3.1 which identified 3 major water types and 10 subtypes. This classification scheme was reorganized by Howard and Beck (1986) and is shown

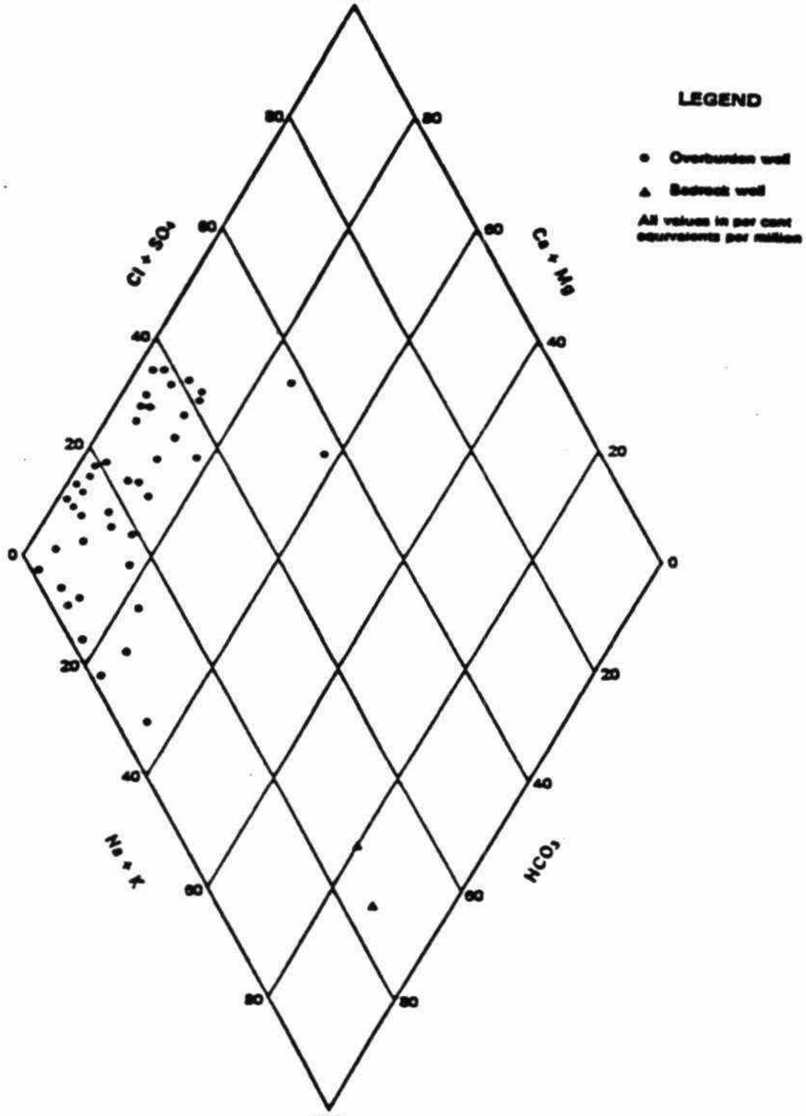


Figure 3.1 Major ion chemistry of groundwaters in the Duffins Creek-Rouge River basins (Sibul et al., 1977)

alongside the original classification in Table 3.1. Essentially, the scheme recognises the transition shown in Figure 3.2 from Ca-HCO_3 dominated recharge waters (Type 1A) to Na(+K)-HCO_3 dominated waters (Type 4A). This chemical

Table 3.1 General Characteristics of Major Water Types in Duffins Creek-Rouge River Basins

Water Type		Description	Parameter						
Original Beck (1985)	New Scheme Howard & Beck (1986)		Ca epm %	Na epm %	Cl mg/L	NO3 mg/L	Cl/NO3	I ug/L	F ug/L
UNCONTAMINATED									
1A	1A	Recharge waters	> 40	< 10	< 5	< 10	---	< 5	< 250
2A1	2A	Immature ion exchange	< 60 < 25	> 10	< 10	< 10	---	< 10	175-300
2A2	3A	Moderately mature ion exchange	< 50 < 50	> 25	< 15	< 10	---	< 20	250-350
2A3	4A	Mature ion exchange	< 35	> 50	< 15	< 10	---	> 15	> 250
CONTAMINATED									
1B1	1S	Chloride enriched	> 40	< 25	> 40	< 10	> 25	< 10	< 150
1B2	1N	Nitrate enriched	> 40	< 50	---	> 10	< 0.5	< 10	< 200
1B, 2B	1,2,3,4U	Nitrate/Chloride enriched	---	---	> 15	> 10	---	---	---
BEDROCK									
3A	B-1*	Sodium bicarbonate	< 30	> 60	> 50	---	---	---	---
3B	B-2*	Calcium chloride	> 20 < 50	> 25 < 50	> 250	---	---	---	---

* new designation not published in Howard and Beck (1986)

behaviour is a natural chemical evolutionary process in which calcium exchanges with adsorbed sodium as the groundwaters move through the aquifer system. Locally, this chemical transition is masked by contamination which elevates the concentrations of chloride, nitrate and their counter cations. Beck concluded that as many as 35 percent of groundwater samples collected during the study were contaminated in this way. Groundwater Types 1B1 and 1B2, subsequently reclassified as Type 1S and 1N by Howard and Beck (1986) (Table 3.1) represent waters characterized by elevated chloride and nitrate concentrations respectively (Beck, 1985). As seen in Figure 3.2, these waters are essentially Type 1A Ca-HCO_3 recharge waters which have been displaced from the Type 1A field as chloride and nitrate ions compete with bicarbonate as the dominant anion. Beck (1985) proposed that the high chloride and nitrate concentrations of the 1S and 1N groundwaters were due to contamination from unnatural sources such as road de-icing chemicals and fertilizers respectively, but he was unable to confirm the sources of enrichment.

Many groundwaters in the study area were found to contain elevated concentrations of both chloride and nitrate. These waters were initially classified by Beck as Types 1B and 2B to indicate that the sources were unknown or undifferentiated. In the new scheme these waters were reclassified 1U through 4U.

Two types of bedrock waters (3A and 3B) were also identified by Beck (1985). Type 3A bedrock waters (reclassified as B-1) are sodium bicarbonate waters with chloride concentrations greater than 50 mg/L, while Type 3B bedrock waters (reclassified as B-2) are calcium chloride waters (Table 3.1). Beck showed that these chloride enriched waters were also enriched in iodide, a chemical characteristic not observed in recharge waters contaminated by road salts. This drew attention to the possible use of iodide as a possible indicator of chloride origin.

3.3 Research on Contaminant Sources

3.3.1 Introduction

Studies in southern Ontario by Beck (1985); Hill (1982); Gillham and Webber (1969), have indicated that a wide range of contaminant sources may be responsible for elevated chloride and nitrate concentrations in groundwaters. These sources include organic fertilizers and manure piles (Gillham and Webber, 1969; Mink et al., 1976), inorganic fertilizers (Hill, 1982; Zaporozec, 1983; Poinke and Urban, 1985; Saffina and Keeney, 1977), road de-icing chemicals (Toler and Pollock, 1974; Paine, 1979; Kelsey and Hootman, 1985), urbanization (Eisen and Anderson, 1979; Ritter and Chirnside, 1984) and landfill leachates. A review of the relevant literature as presented below can provide a valuable insight into the nature and chemical character of many of these potential chloride sources.

3.3.2 Road de-icing chemicals

3.3.2.1 Introduction

In Canada and the northern states of the U.S., a major potential source of chloride enrichment in groundwater is the application of road de-icing chemicals to highways and roads during the winter months. When road de-icing chemicals are spread on a snowy road surface, the salts dissociate into ions. The result is a solution which has a freezing point considerably below 0°C, the freezing point of pure water. During its melting action, the solution becomes increasingly dilute; eventually melting ceases. The factors which in-

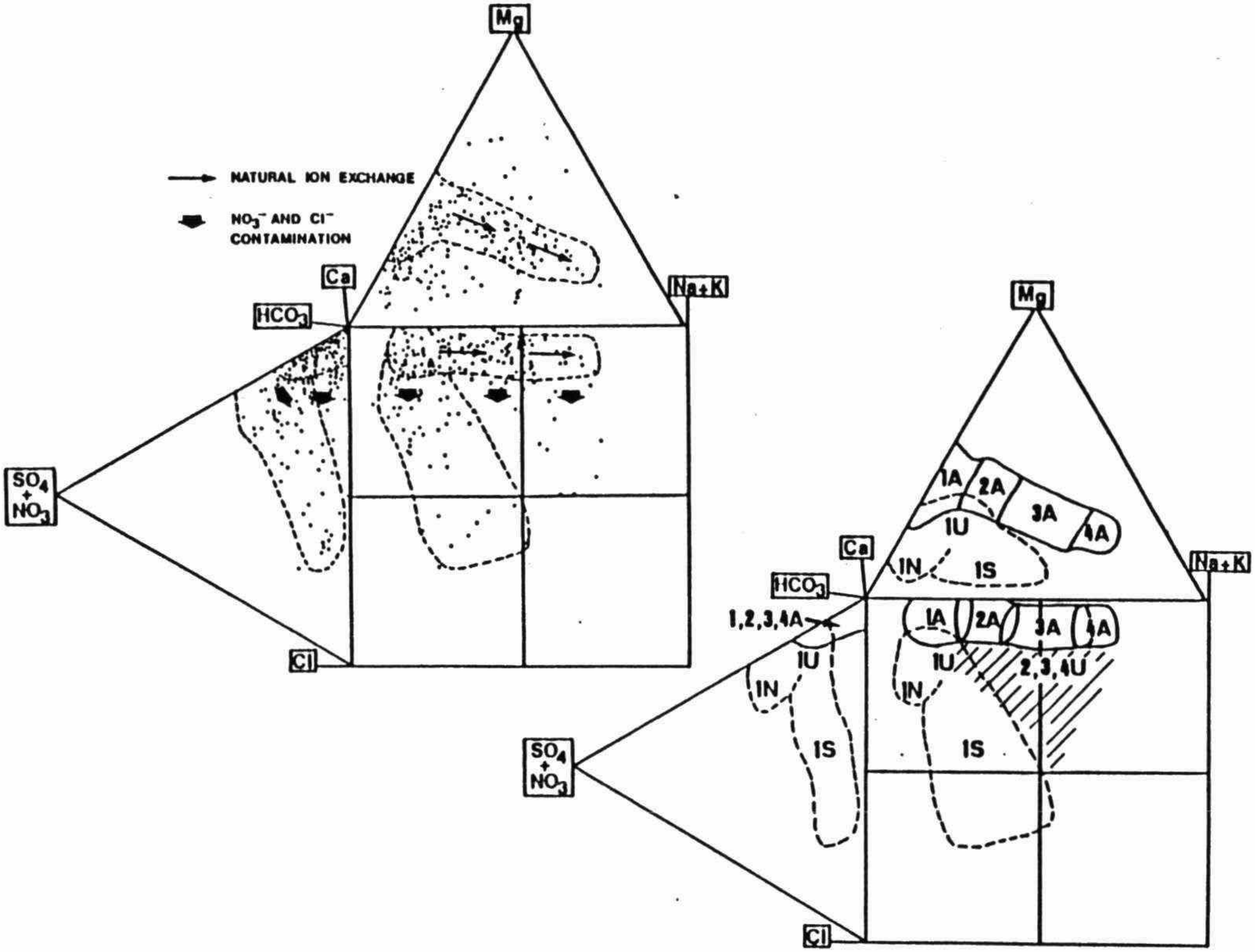


FIGURE 3.2 Hydrochemical classification of groundwaters in the Duffins Creek-Rouge River basins (Howard and Beck, 1986)

fluence melting are 1) air and pavement temperature; 2) traffic; 3) amount of solar radiation; 4) humidity; 5) wind; 6) type of road surface; and 7) topography (Hanley, 1979). Road de-icing chemicals are most effectively utilised before a snowstorm to create a thin layer of salt solution which discourages or weakens bonding between the snow and the road. This prevents compaction of the snow and ice and facilitates its removal by snow ploughing (Hanley, 1979).

3.3.2.2 Types of chemical road de-icing chemicals

Road de-icing chemicals take several forms and are applied in many different ways. The two types of de-icing chemicals which are preferred for use on Ontario roads are sodium chloride and calcium chloride (Table 3.2). These chemicals may be used in a pure chemical form but are also used in conjunction with abrasives such as sand. In the Municipality of Metropolitan Toronto, the Works Dept. applies pure sodium chloride to main urban roads, while sodium chloride or mixtures of sand and (5 percent) sodium chloride are used on side streets. Mixtures of 5 percent sodium chloride and sand are also used on gravel roads as pure sodium chloride tends to cause potholing of the road surface during a thaw (Beck, 1985).

Table 3.2 Common Types of Road De-icing Chemical

Type	Formula	Description
SODIUM CHLORIDE	$NaCl$	- is the most commonly used chemical de-icer - translucent, clear, granular form - effective at temperatures above -18°C - below -12°C it is no longer cost effective
CALCIUM CHLORIDE	$CaCl_2$	- opaque, white, used in pellet form - most effective at temperatures between -12°C and -34°C

Calcium chloride is not as frequently used as sodium chloride because it two to four times more expensive and makes the road surface slippery when wet (Hanley, 1979). Municipalities such as Ajax have used a mixture of sand and calcium chloride with success, finding that 50 percent less salt is required and that the melting action of the salt is increased to temperatures below -20°C (Fabricius and Whyte, 1980).

3.3.2.3 Chemical behaviour of road salt in the unsaturated zone

Very little is known about the behaviour and fate of de-icing chemicals applied to roads and highways. Williams and DeGroot (1977) estimated that for 1975-76, 1.5 X 10^6 tons of road salt in the form of sodium chloride, calcium chloride, or mixtures of these chemicals with abrasives were applied to Ontario roads and highways. During a single winter snowstorm in southern Ontario in 1987 an estimated 2200 kg of road de-icing chemicals were applied to the roads of Metropolitan Toronto. A study of the Don River in 1979 by Paine indicated that only 50% of chloride applied in the form of road de-icing salts is flushed from the catchment on an annual basis suggesting that the remainder enters the soil and groundwater.

Several hydrogeological investigations (e.g. Toler and Pollock, 1974; M.O.E., 1979) have determined that road de-icing chemicals are responsible for the contamination of groundwater. Studies by Toler and Pollock (1974) in Chelmsford, Massachusetts have shown that road de-icing chemicals applied to highways accumulate in the unsaturated zone until they reach a stable quasi-equilibrium concentration. This is in contrast to their effect on groundwater, where a positive correlation was found between concentrations of chloride in the groundwater and the amount of road salt applied each year.

In Canada, several studies have demonstrated that road de-icing chemicals may be causing severe environmental impact, and involve the degradation of groundwater quality. However, most of these studies have focused on point source contamination such as salt storage piles and snow dump sites. For example, Scott (1980) demonstrated that soil adjacent to snow dump sites in Metropolitan Toronto is accumulating sodium, chloride, and lead. Surface runoff from such sites contained chloride and sodium concentrations as high as 1970 mg/L and 1200 mg/L respectively. No other chemical parameters were investigated.

3.3.3 Sources of nitrate contamination

3.3.3.1 Introduction

Sources of nitrate contamination are both natural and man-made. Natural sources include organic nitrogen originating from the decay of organic detritus. Under aerobic conditions, such as caused by deep ploughing of the soil, this nitrogen is quickly converted to its highly mobile nitrate (NO_3^-) form and leached by recharging groundwaters. Unnatural sources include acid precipitation and septic tank sewage; however, the most common form of nitrate pollution of groundwater is the application of organic and inorganic fertilizers.

3.3.3.2 Inorganic fertilizers

During their growth, plants such as corn, tobacco, soybean and vegetables, absorb a large number of macro- and micro- nutrients from the soil and interstitial pore waters. To maintain high production yields, these nutrients which include phosphorous, nitrogen, potassium, calcium, boron, copper, iron, and manganese (Webber, 1982), can be replaced by the regular application of inorganic and organic fertilizers. On modern farms, inorganic chemically manufactured fertilizers account for over 95% of the total fertilizer consumption (Pratt, 1965).

Each year in Ontario, approximately 815,000 tonnes of inorganic fertilizer are applied by farmers to agricultural land (Webber, 1982). There are many different types of inorganic fertilizers available and the type chosen is dictated by soil characteristics, type of crop to be grown, and the method of crop management to be implemented (Webber, 1982). Fertilizers are classified according to three primary soil macronutrients: phosphorous, nitrogen, and potassium. A brief description of each type is summarized in Table 3.3.

Table 3.3 Inorganic Fertilizer Materials

Type	Name	Description
NITROGEN	Anhydrous Ammonia (NH_3), 82% N	- a colorless, inflammable gas
	Aqua ammonia ($NH_3.H_2O$), 20% N	- ammonia dissolved in water, kept under low pressure
	Nitrogen solutions 28 - 41% N	- 28 to 32% N materials made by dissolving urea and ammonium nitrate in water - 41% N solution contains urea ammonium nitrate, ammonia
	Urea ($CO(NH_2)_2$), 46% N	- white, prilled, usually plowed into soil
	Ammonium nitrate (NH_4NO_3)	- white, prilled, half of N in ammonium form, half in nitrate form
PHOSPHOROUS	Ordinary superphosphate	- consists of 18 - 20 % P_2O_5 or 8.7% P - made by treatment of rock phosphate with sulphuric acid - contains 48% calcium sulfate
	Concentrated or triple phosphate	- consists of 44 - 46% P_2O_5 or 20.1% P - made by treatment of rock phosphate with phosphoric acid
	Ammonium phosphates	- produced by ammoniation of phosphoric acid
POTASH	Potassium chloride (KCl) 60% K_2O or 50% K	- most common K fertilizer
	Potassium sulfate (K_2SO_4) 50% K_2O or 41% K	- used for crops in which quality is adversely affected by chloride

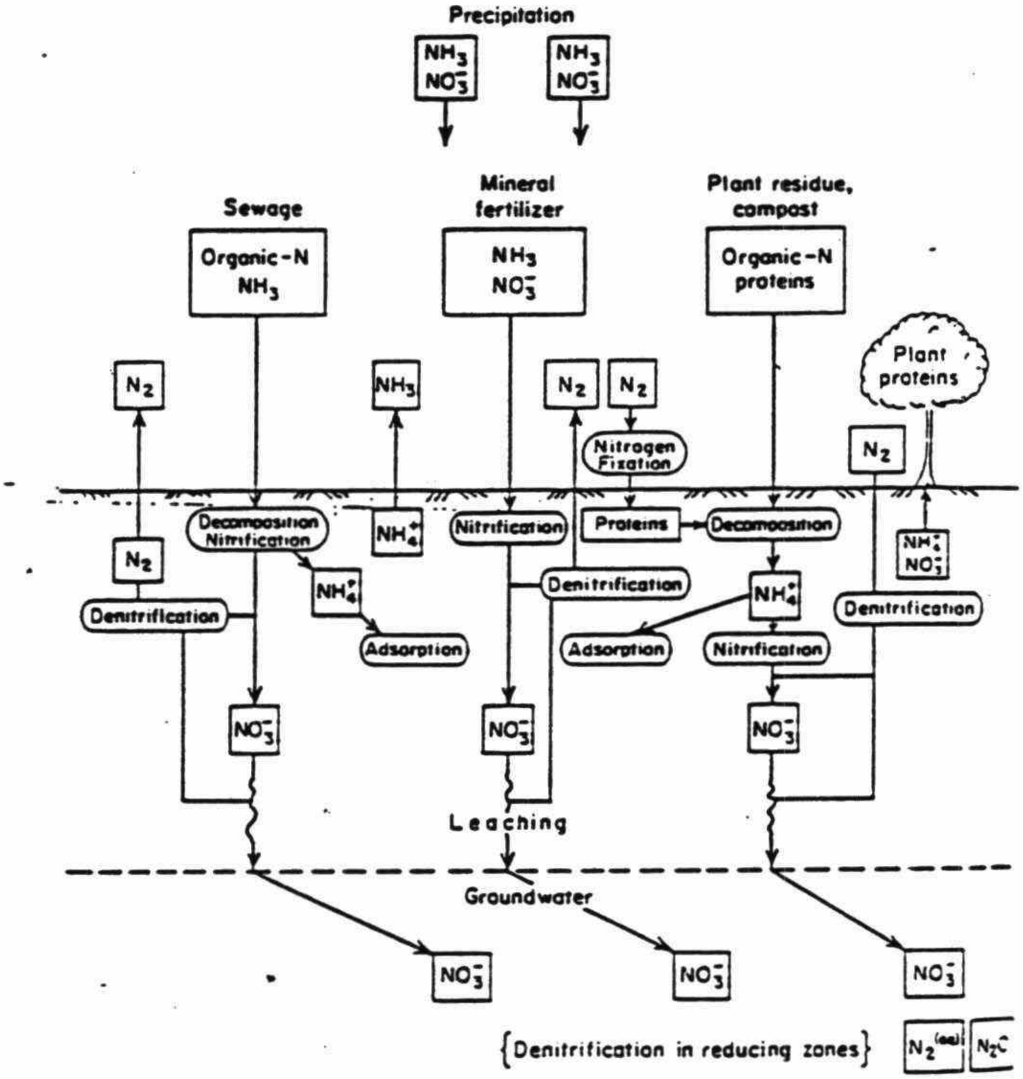


Figure 3.3 The nitrogen cycle (Freeze and Cherry, 1979)

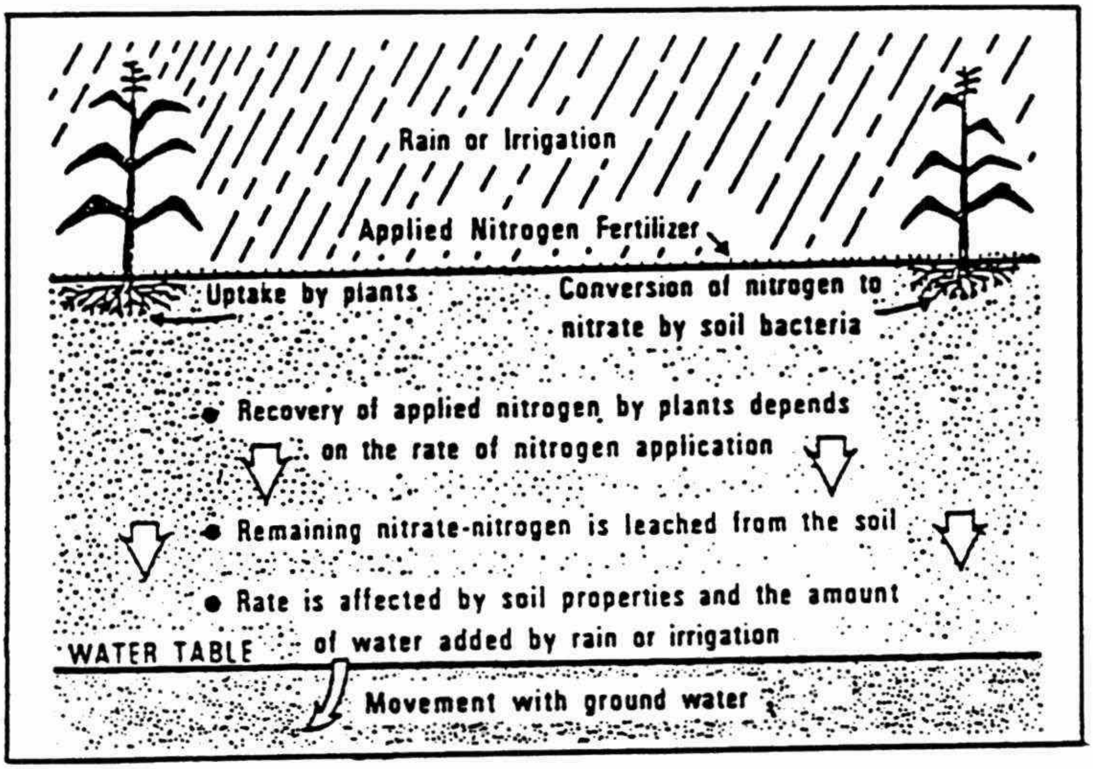

Rain or Irrigation
Applied Nitrogen Fertilizer
Uptake by plants
Conversion of nitrogen to nitrate by soil bacteria
• Recovery of applied nitrogen by plants depends on the rate of nitrogen application
• Remaining nitrate-nitrogen is leached from the soil
• Rate is affected by soil properties and the amount of water added by rain or irrigation
WATER TABLE
Movement with ground water

Figure 3.4 The pathway of nitrogen fertilizer in the unsaturated zone (Zaporozec, 1983)

3.3.3.3 Organic fertilizers

With more than 90 million farm animals and poultry in southern Ontario, it is estimated that about 34 million metric tons of manure are produced each year (Webber, 1982). Organic fertilizers are used in two forms; 1) as liquids or 2) as semi-solids with bedding materials. In Ontario, livestock manure is usually handled as a semi-solid with bedding, while hog and poultry manure is in liquid or slurry form. Bedding material is commonly cereal straw, wood shavings, or sawdust. Solid manure may be stored in the open, or covered in the feedlot or pen. Liquid manure may be placed in anaerobic storage to allow anaerobic and facultative bacteria to convert organic solids to liquids and gases. Storage may also be under aerobic conditions allowing the liquid manures to biodegrade in the presence of dissolved oxygen (Webber, 1982).

In addition to livestock manure, sewage sludge may also be used as a soil fertilizer. Raw sewage from septic tanks and municipal areas was once frequently spread on agricultural land in Canada and the United States. However, this practice was discontinued due to the potential health dangers from the raw material. Instead, sewage sludge which is digested, and dried sewage solids are often used today (Webber, 1982).

3.3.3.4 Chemical behaviour of fertilizers in the unsaturated zone

To determine whether chloride enrichment in groundwaters is the result of contamination by fertilizer materials, it is important to understand the chemical behaviour of fertilizers in the unsaturated zone. Since fertilizers are applied annually, it would be expected that many of the fertilizer constituents would migrate through the unsaturated zone into groundwater. However, while some studies show that specific constituents can leach through the subsurface, there are indications that other constituents may have restricted mobility for various physio-chemical reasons.

The major component of applied inorganic fertilizers is nitrogen. When nitrogen is added to the soil, the processes of ammonification and nitrification occur as shown in Figure 3.4. Depending on the amount of fertilizer applied, only a certain portion of the nitrogen is recovered by the growing crops, while the remaining nitrate leaches through the unsaturated zone. The rate of leaching is determined in part by soil properties, the climate and the application rates of fertilizer and irrigation water. Because of its anionic form and the lack of solubility constraints, nitrate is very mobile in groundwater. Nitrate is not a thermodynamically stable form of nitrogen, and may be reduced by the process of denitrification to N_2O or N_2. This process can occur if there are sufficient quantities of organic matter and denitrifying bacteria present (Freeze and Cherry, 1979) and has been used to explain low nitrate concentrations in the deeper part of an aquifer underlying cropland (Gillham and Cherry, 1978).

It is well known that the other primary constituents of fertilizer, phosphorous and potassium, are both relatively immobile in the subsurface. In the case of potassium, this is due to the ions' ability to undergo cation exchange

(Freeze and Cherry, 1979). Phosphorous in the form of H_2PO_4 and HPO_4 ions is strongly adsorbed to soils (Brady, 1974) primarily by anion adsorption reactions on sesquioxide surfaces (Hingston et al., 1967; Sawhney and Hill, 1975). A study by Wiklander (1976) determined that phosphate anions had the greatest adsorptivity according to the order $HPO_4 > H_2PO_4 > SO_4 > NO_3 = Cl$. This study also noted that with phosphate adsorption, cations such as K, Mg, and Ca were retained, indicating that the cation exchange capacity of the soil increases with phosphate adsorption. Phosphate ions also undergo several precipitation reactions (Johnson and Cole, 1980). The most important of these reactions is precipitation by soluble iron, aluminum, and manganese ions. As a consequence of these processes, phosphate tends to be an extremely immobile anion in soils.

The fate of many of the trace constituents or micronutrients of inorganic fertilizers in the unsaturated zone remains largely uninvestigated. Most studies have focused on the accumulation of specific trace constituents of fertilizers such as zinc (Brown et al., 1964), iron, manganese and copper (Follet and Lindsay, 1971) in soils and in crops grown on these soils. For example, much work has been conducted on the accumulation of cadmium resulting from the application of phosphate fertilizers to cropland. Studies conducted by Williams and David (1976) found that phosphate fertilizers contain appreciable amounts of cadmium and zinc of which only a small amount is utilized by growing plants. Despite the small amounts of cadmium used by plants, most of the remaining cadmium and zinc was found to be relatively immobile in the unsaturated zone. At least 85% of fertilizer cadmium was retained in the cultivated layers of the soil with at least 80% of the accumulated cadmium exchangeable with ammonium ions. Mortvedt and Osborn (1982) determined that Cd is present in triple superphosphate and diammonium phosphate as $Cd(H_2PO_4)_2$ and/or $CdHPO_4$. Further work is required to determine the fate of other trace constituents in fertilizers.

Considerable research has been conducted into the accumulation, movement, and distribution of the heavy metal fraction of sewage sludge, which is applied as a fertilizer, in the soil profile (Williams et al., 1980; Andersson and Nilsson, 1972). The study by Williams et al. (1980) involved the application of up to 225 metric tons/ha of sewage sludge to field plots. It showed that regular, annual applications of sludge tends to increase the trace metal soil concentrations of Pb, Cu, Cd, Cr, Fe, and Zn, while concentrations of Mn, Ni, and Co were not affected. It was also shown that the accumulation of trace metals was limited to the depth of tillage. This is partly because the metals exist in a relatively immobile form in the sludge and also because there are many materials present in soils which are capable of immobilizing heavy metals including clays, hydrous oxides of iron and manganese, carbonates, organic matter, fulvic and humic acids, and inorganic chemical compounds. Zinc adsorption was found to be related to the clay content and the presence of organic matter, while copper adsorption was found to be closely associated with the humic acid fraction of the soil and strongly complexed (Williams et al., 1980).

3.3.3.5 Nitrate contamination of groundwater - Case Studies

There are many examples in which nitrate contamination of groundwater has been associated with agricultural activities (e.g. Zaporozec, 1983; Gustafson, 1983; Poinke and Urban, 1985; Saffigna and Keeney, 1977). Other than chloride, which appears in moderately enhanced concentrations, few other fertilizer macro-nutrients (such as phosphate and potassium) are normally observed in anomalous concentrations beneath agricultural lands. While in part, this may be explained by chemical adsorbance of phosphate and potassium by clay minerals, it is also possible that fertilizers are not always the primary source of the nitrate contamination.

Researchers investigating the problem of groundwater quality degradation beneath cropland have attempted to use ions other than Cl and NO_3 as indicators of fertilizer contamination without much success. Other ions considered include the cations, Na, Mg, Ca, and K whose value as diagnostic source indicators is inhibited by their tendency to be sorbed by soil colloids (Poinke and Urban, 1985). However, the ratios NO_3-N/Na and NO_3-N/Cl have been used with limited success by Wagner et al.(1976); and Saffigna and Keeney (1977). Saffigna and Keeney (1977), for example, determined that a value of 4.0 for the concentration ratio NO_3-N/Cl represents overapplication of K, N, P fertilizer as compared to a baseline of 0.8 to 2.5 representing normal environmental conditions.

Although considerable research on nitrate contamination of groundwater is now being conducted, very little data generally exist for Canada, and, in particular for south-central Ontario where intensive agricultural practices are carried out. Two studies in the north-eastern United States and one in Ontario, bear some important implications for this study.

Results of a seven year groundwater study undertaken in the community of Twelve Pines, Long Island, New York has shown that a significant increase in the concentration of nitrate from an average of 0.06 mg/L (N) in 1972 to 1.4 mg/L (N) in 1979 has occurred. Prior to 1970 the study area was uninhabited but by 1978, the population was 1700 and the average fertilizer application rate was 107 kg/km^2/yr representing an annual load of 3870 kg of N (Flipse et al., 1984). Flipse et al. considered several nitrogen sources including fertilizers, precipitation, irrigation water, animal wastes, and subsurface migration from upgradient areas. However, on the basis of the nitrate - nitrogen ratio $^{15}N/^{14}N$ they concluded that the source of the nitrate was lawn fertilizer rather than human or animal wastes. Although the Twelve Pines study considered only a small number of chemical parameters (total ammonium, organic nitrogen, nitrate) and nitrate-nitrogen isotopes, it has important implications for this study. The Twelve Pines area obtains groundwater supplies from medium to coarse grained glacial sand and gravels (where the water table is approximately 12 m below surface) similar to glacial sediments in south-central Ontario, and demonstrates i) the serious effects of fertilizer application over a short period of time and ii) the potential risks associated with domestic use of fertilizer.

In the central Ontario study, Hill (1982) determined that commercial nitrogen fertilizer is a major source of nitrate in the groundwater of the Alliston area. Elevated concentrations of nitrate-nitrogen (> 10 mg/L NO_3-N) were measured in groundwaters under potato fields heavily fertilized with KCl and ammonium nitrate, while groundwater beneath pastureland and forest contained less than 1 mg/L. A positive correlation (r=0.76) was found between the average rate of fertilizer application and the concentration NO_3-N in groundwaters. This study suggests a potential indicator in the form of Cl/NO_3-N ratio for groundwaters contaminated by inorganic fertilizers containing KCl. These waters had Cl/NO_3-N ratios between 1:1 and 2.5:1.

3.3.4 Urban Development

3.3.4.1 Introduction

The land surrounding Metropolitan Toronto including the land in the Duffins Creek-Rouge River basins is undergoing rapid urbanization. Since many of these areas currently obtain potable water supplies from shallow aquifer systems in glacial sediments, the potential effects of urbanization on groundwater quality represents an important concern.

3.3.4.2 Previous Investigations

Most studies investigating the effects of urbanization on water quality have been concerned with the potential impact on surface water quality rather than on groundwater quality. One exception is a study conducted in the Menomonee River Watershed near Milwaukee, Wisconsin by Eisen and Anderson, 1979. The Menomonee River Watershed is characterized by a heavily urbanized southern half, which includes Milwaukee, while the northern half of the watershed is suburban to rural. There are two aquifer systems in the watershed; an upper aquifer system consisting of sand and gravel aquifers within glacial drift (thickness varies from 15 m to 80 m) and a lower bedrock aquifer system consisting of two confined aquifers. Data from this study show that elevated concentrations of ammonium, sulphate and chloride are the main products of urbanization. (Groundwater in the Wisconsin-Lake Michigan Basin is calcium bicarbonate dominated). This trend of elevated chloride and sulphate concentrations in groundwater as a result of urbanization has been noted by several other researchers (for example, Long and Saleem, 1974). Eisen and Anderson (1979) attributed some of the elevated chloride to infiltration of road salt based on the proximity of sampling sites to major highways. The remainder of the chloride, the elevated sulphate and ammonium concentrations, and the presence of fecal coliform and fecal strep bacteria, suggested that the source of the contaminants was sewage from leaky sewer lines and/or infiltrating polluted river water. Eisen and Anderson (1979) found that heavy metals such as zinc, copper and cadmium were at or below detection limits while phosphate and nitrate concentrations were generally below 0.02 mg/L and 0.015 mg/L respectively.

3.3.5 Landfill leachates

3.3.5.1 Introduction

Considerable concern has been expressed over contamination of groundwater from municipal landfill sites, particularly those older sites which were installed with little consideration for monitoring and leachate control. Leachate refers to the liquid generated by a landfill, usually as a result of infiltrating water, including groundwater, interacting with the decomposing waste. Frequently, the leachate contains suspended matter, pathogens and very high concentrations of dissolved chemicals. It only becomes a concern when it migrates from the landfill, usually by sub-surface flow, where it can cause serious degradation of groundwater quality (Freeze and Cherry, 1979).

Ideally, it should be possible to distinguish groundwater contamination by leachate migration from the many other contaminant sources. However, studies indicate that this is an extremely difficult problem (e.g. Qasim and Burchinal, 1970), primarily because landfill leachates have a highly variable chemical composition. In a study of 123 landfill leachates, Clark and Pisken (1976) (Table 3.4) determined that the metals boron, zinc, copper, and iron were present in variable but considerably elevated concentrations relative to

Table 3.4 Concentrations of inorganic constituents in landfill leachates from Illinois landfill sites*

Parameter	Concentration Range (mg/L)
Arsenic	0.000 - 40
Barium	0.2 - 9.0
Boron	0.42 - 70
Cadmium	0.00 - 1.16
Calcium	23 - 3050
Chloride	31 - 4350
Chromium	0.00 - 22.5
Copper	0.00 - 1100
Fluoride	0.1 - 1.3
Iron	0.9 - 42000
Lead	0.00 - 6.6
Magnesium	12 - 1102
Manganese	0.00 - -
Nickel	0.0 - 1.7
Nitrate	0.0 - 1.8
Phosphate	0.00 - 52
Potassium	2 - 1920
Selenium	ND
Sodium	15 - 8000
Sulphate	0 - 84000
Zinc	0.0 - 250

* after Clark and Pisken (1976); ND = not detected

other trace constituents analyzed. However, as shown in the table, these parameters are highly variable, and may have limited diagnostic use.

The search for diagnostic indicators of groundwater contamination by landfill leachate is seriously complicated by the chemical modification it undergoes during sub-surface migration. Only chloride is transported with minimal alteration, a reason this ion is frequently used to map the extent of a leachate plume. The remaining chemical constituents are modified to varying extents during leachate movement, a subject which has been studied by several workers (e.g. Cherry et al., 1985 and Korte et al., 1976). Korte et al. conducted experiments with a natural leachate which was added to soil columns containing a wide range of different soil types. Concentrations of Cu, Pb, Be, Zn, Cd, Ni, Hg, Se, V, As, and Cr were measured. It was found that copper, beryllium and lead were the least mobile. Selenium, vanadium, arsenic, zinc, cadmium, nickel, mercury and chromium had the greatest mobility in sandy soils but were strongly retarded in clayey soils. They concluded that the percent of clay in the soil was the single most important factor in predicting whether trace metals will be transported during leachate migration.

3.3.6 Review

Considerable research has been conducted on many potential contaminants of groundwaters. Since much of the work involves intensive water quality monitoring, sometimes over a period of several years, emphasis tends to be placed on measuring only a few chemical parameters such as chloride, nitrate-nitrogen, ammonium, and phosphate. Very few hydrogeological investigations have focused on measuring trace constituents with the intent of identifying potential chemical indicators of contamination. Instead, trace element research of chloride enriching contaminants, particularly fertilizers, has primarily considered the effects of metals on soil quality and on plant uptake.

The hydrogeological study described in this report has attempted to address this important issue through comprehensive multi-parameter inorganic chemical analysis of a wide range of potential contaminants, both in their raw states at source, and following sub-surface transport. In this way, it has been possible to identify parameters which may be useful as diagnostic indicators of source origin.

4. DESCRIPTION OF HYDROCHEMICAL METHODOLOGY

4.1. Introduction

It is clear from the discussion and studies presented in Section 3, that the detection and identification of contaminant origins is severely complicated by a number of factors. These range from the chemical changes the contaminants undergo as a result of rock-water interaction to the effects of mixing with uncontaminated groundwater. The former processes can completely modify the chemical characteristics of the contaminants, the latter process can dilute the contaminants to barely detectable concentrations.

Faced with these difficulties, a three phased approach was adopted. In the first phase, a regional multi-parameter hydrochemical study was conducted in order to determine the background major ion, minor ion and trace element characteristics of naturally evolving groundwaters. The second phase involved comprehensive chemical analysis of the potential source contaminants, and the third phase focused on the chemical characteristics of the contaminants in the shallow sub-surface. In addition to providing information on the chemical modification of the contaminants by rock-water interaction, the third phase also provided an indication of the degree to which contaminants are accumulating in the shallow sub-surface.

A description of all the analytical techniques is contained in Appendix I. Analytical results for the well waters, contaminants, interstitial waters and the sediments are listed in Appendices II, III, IV, and V respectively. Section 4.2 describes the collection and processing of well water, interstitial water and contaminant samples: Section 4.3 describes the quality control measures used in the present study.

4.2 Description of Sample Survey

4.2.1 Well Water Samples

4.2.1.1 Introduction

To determine background levels of anion, major cation and trace constituents in uncontaminated, naturally evolving groundwaters, domestic well waters were sampled from the Rouge River-Duffins Creek drainage basins. A total of 107 wells were sampled and the sample locations are shown in Figure 4.1. For ease of cross-reference, well identification numbers are identical to those used in a similar study by Beck (1985). Beck's study involved a slightly larger number samples but his analysis was restricted to anions and major cations.

4.2.1.2 Collection and Handling of Well Water Samples

All the well water samples were collected from domestic wells, usually from an outside tap which bypassed filtering and/or water softening systems. Sampling priority was given to pumped and naturally flowing wells for which water well records were confidently known. To minimise the risk of contamination by the

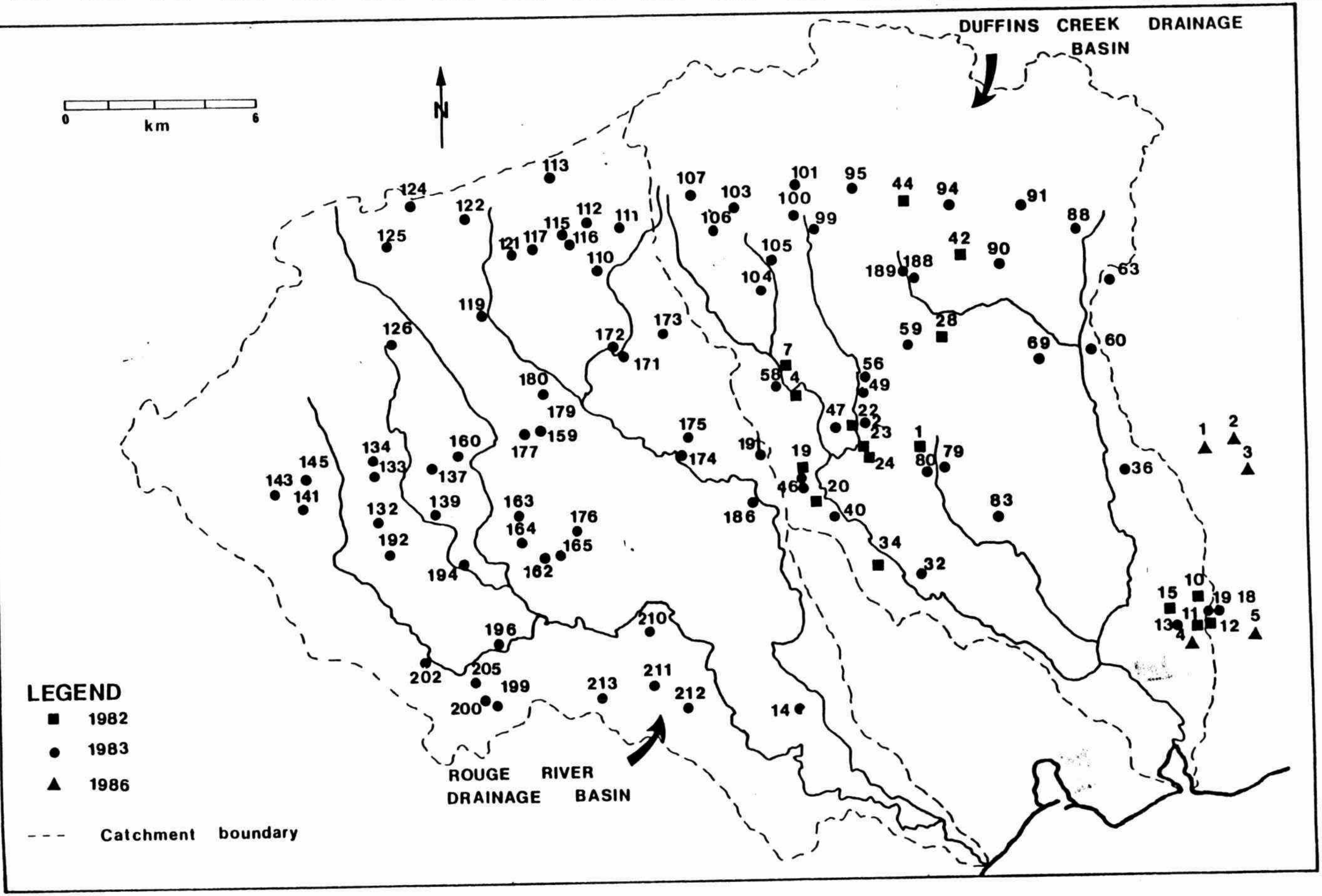


FIGURE 4.1 Water well sample location map

pump and well installation, sampling taps were run for an extended period of time prior to sample collection. In this way, water samples were obtained directly from the formation. The results of the trace metal analyses seem to indicate, that this endeavor was successful.

Samples were collected in polyethylene sample bottles that had been washed and rinsed in a 10 per cent nitric acid bath, followed by 3 separate rinses with distilled water. The sample bottles were then stored filled to the brim with distilled water and sealed. The bottles were emptied immediately prior to use.

During sample collection, the sample bottle was rinsed 3 times with well water to displace any distilled water remaining in the bottle. Two 250 mL samples were collected at each site; sampling techniques differed according to the type of analysis required. The sample for trace element analysis was immediately filtered and acidified in the field to preserve metals and metalloids for trace constituent analysis. Filtering was achieved under pressure using a 30cc hand pump attached to a Sartorius polycarbonate filtering apparatus. To avoid the risk of contaminating samples during filtering, the 0.45um cellulose acetate filter membranes were washed immediately prior to use with 0.1 % *Ultrapure* nitric acid and rinsed 3 times in double distilled water. The 250 mL sample for anion and major cation analysis received less rigorous attention. The sample was not filtered in the field unless particulate matter was obviously present. Otherwise the only precaution taken was to exclude all air from the sample bottle before sealing. Both samples were packed in ice for transportation to the laboratory.

83 of the 107 well water samples were submitted for complete anion and major cation analysis in the University of Toronto Groundwater Research laboratory. Preference was given to pH and alkalinity measurements which were determined within 8 hours of sample collection. Other parameters were measured as urgently as possible (see Appendix I).

Samples from all 107 sites were analysed for trace metal parameters using inductively coupled plasma-atomic emission spectrometry or ICP-AES. The 250 mL sample volume permitted sample preconcentration which improved the level of determination ten-fold. The preconcentration technique and the ICP analytical method are described in detail in Appendix I.

4.2.2 Analyses of Potential Contaminant Sources

Forty-two samples of bedrock waters and a wide variety of common contaminant sources including fertilizers and road de-icing chemicals were collected and analysed during the study. Here, the primary aim was to identify chemical parameters which could prove useful as diagnostic indicators of source. The sample locations are shown in Figure 4.2. Details of the samples and analytical results are provided in Appendix III.

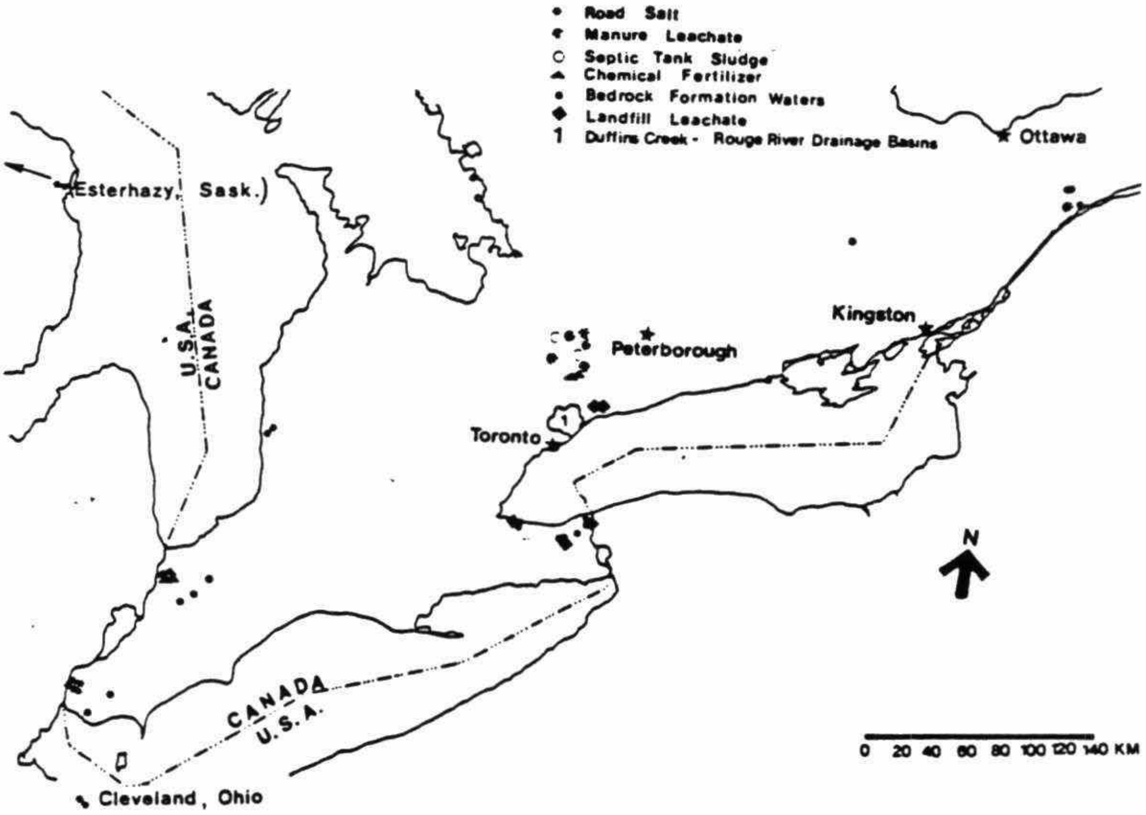


FIGURE 4.2 Contaminant source location map (Beck and Howard, 1986)

Types of contaminant sample collected included:

- Road de-icing chemicals

  Ten samples of road salt (NaCl) and 1 sample of $CaCl_2$ were collected from 4 different salt suppliers. All but two of the samples had been obtained from the Salina Formation which is a Silurian age evaporite sequence. Two of the eleven samples had been obtained from Saskatchewan and were by-products of potash mining operations. All the samples analysed contained 0.5 to 1.0 cm granules mixed with minor amounts of sand.

- Inorganic fertilizers

  Four samples of inorganic fertilizer were obtained from Canadian Industries Limited (CIL) in Courtright, Ontario. These included mono-, and di- ammonium phosphates, prilled urea, and ammonium nitrate.

- Sewage sludge and manure

  A total of nine samples of various sludges and manure leachates were sampled. These included chicken, horse, pig, dairy cow manures and a septic tank sludge. They were sampled from various locations including a liquid holding tank, manure pit, manure spreader and a weathered manure pile.

- Landfill leachates

  Five landfill leachates were obtained from leachate collection systems at the Mountain Road, Glenridge Quarry, and Brock West landfill sites.

- Bedrock waters

  To investigate chloride "contamination" from natural, non-point geological sources, such as bedrock waters, a total of fourteen locations were sampled. Many of these water samples could be classified as brines and were collected at various Ontario locations (see Figure 4.2).

4.2.3 Collection and handling of contaminant samples

Contaminant and bedrock water samples were collected as a co-operative effort between the University of Toronto Groundwater Research Group and Hunter and Associates. Procedures for the collection, handling and preparation of the samples depended on the nature of the material collected. Fluids were collected in two 250mL sample bottles which were packed in ice for transportation to the University of Toronto laboratories. If possible, one sample was filtered and acidified with *Ultrapure* nitric acid for ICP-AES analysis. The other sample was filtered for anion and major cation analysis. Due to the nature of the samples, filtration was normally carried out using a Whatman No. 4 filter. Since only small volumes were generally available, samples were not pre-concentrated prior to analysis.

The solid contaminant samples, which included the road salt and inorganic fertilizers, were made into 5% and 10% solutions respectively. While these solutions were adequate for most analyses, the NaCl road salts required a 1000 times dilution to avoid instrumental interference. (Na concentrations > 20,000 mg/L tend to inhibit the nebulizer function in the ICP-AES to the extent that the measurement of other elements is unreliable).

4.2.4. Sediment and Interstitial water samples

4.2.4.1 Introduction

Since the third objective of the study was to confirm the accumulation of non-point source contamination in the shallow subsurface environment, an interstitial water sampling program was implemented. Interstitial waters were collected from sediments sampled from three sites in Metropolitan Toronto, two sites in the Rouge River basin, one site 2 km north of the basin at Ballantrae and one site located 2.5 km east of Brantford (see section 2.2). A summary of details for each site is provided in Table 4.1.

Table 4.1 Auger Sites

Site	Location	Auger Hole Number	Contaminant
A	Don Valley adjacent to the Parkway	2,3,4,5 6,7,9,23	Urbanization/Road Salt
B	Don Valley Seton Park	1,10	Urbanization/Road Salt
C	Don Valley Snow Dump	8,19,20, 21,22	Urbanization/Road Salt
D	Fourteenth Avenue (Milliken)	11,12,13	Fallow Field/Control Site
E	Ballantrae-Hwy 48	14,15	Road Salt
F	Markham	16	Cropland/Nitrogen Fertilizer
G	Brantford	25,26,27	Cropland/Nitrogen Fertilizer

Sites A, B, and C (Figure 4.3) were carefully located in the Don Valley in East Metropolitan Toronto to allow a range of point and non-point urban contamination sources to be investigated. The soils at sites A, B, and C comprised fill material which dates back to the construction of the Don Valley Parkway. The soils can be broadly classified as dark brown sandy loams.

Site A was represented by two groups of holes located adjacent to heavily traveled urban roads which receive large quantities of salt during winter periods. Sediment samples were obtained from a group of six shallow holes (1.35 to 2.65m depth) drilled beneath an urban bridge, and a group of four shallow holes (0.6 to 3.3m depth) approximately 100m downslope from a ramp on the Don Valley Parkway.

Site B was located at Seton Park on the northwest side of the Don Valley Parkway to provide an urban control site. Sediment samples were collected from two shallow holes (1.2 to 1.8m depth).

Site C was located at a City of Toronto snow dump (Figure 4.3) where sediments were sampled at five locations to investigate whether road de-icing chemicals and heavy metals present in urban street snow are accumulating in shallow subsurface waters.

As a non-urban (suburban) control site, Site D was located in a fallow field on Fourteenth Avenue near Milliken (Figure 4.4). Sediment samples were obtained from three holes drilled to a depth of 1.45 to 2.27m. These holes penetrated Markham clay.

Site E was located 8.8 km north of Stouffville on the west side of Highway 48 (Figure 4.5) in the small community of Ballantrae. It was chosen to determine whether road de-icing chemicals are accumulating in the shallow sub-surface environment adjacent to a heavily salted rural road. Road salt contamination had been implicated in (at least) two domestic wells located on the west side of Highway 48. Both wells showed chloride concentrations in excess of the 250 mg/L maximum desirable limit set by the M.O.E., one of the wells showing a concentration of 1000mg/L. Sediments were sampled from two holes drilled to a depths of 2.69 and 4.3m.

Sites F and G were chosen to investigate the extent and nature of contamination by fertilizers. Site F was located in a cornfield south of Markham (Figure 4.6) while Site G was located in a cornfield 2.5km east of Brantford (Figure 4.7).

4.2.4.2 Collection and handling of sediment and porewater samples

Sediment samples were collected using the following procedure. A gasoline powered auger, Dig-R-Mobile was used to drill to the desired sample depth. The auger rods were then removed and a hand operated auger was used to obtain a partially saturated sediment sample. This sample was placed in a polyethylene bag, sealed, labelled, and packed in ice for transport to the laboratory.

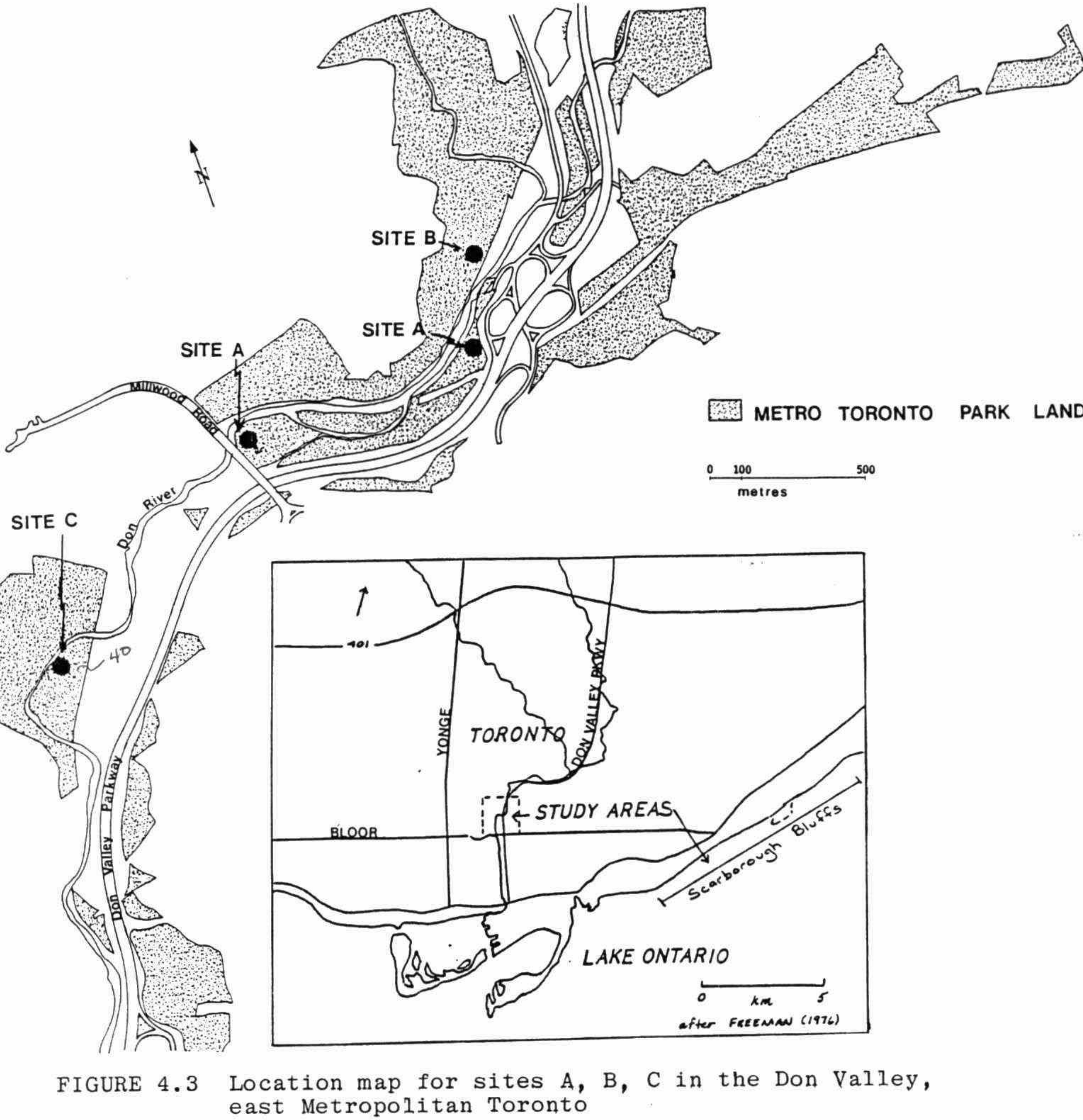


FIGURE 4.3 Location map for sites A, B, C in the Don Valley, east Metropolitan Toronto

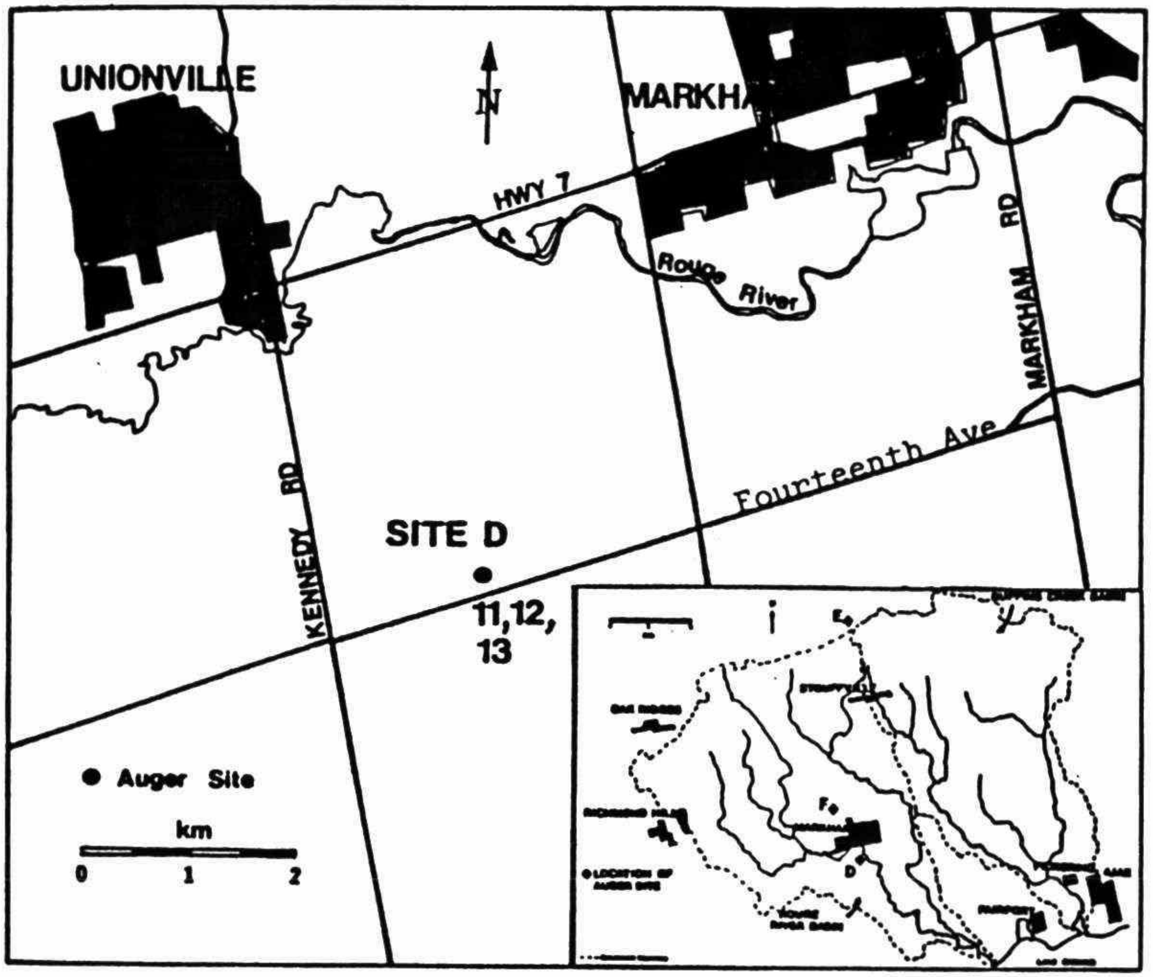


Figure 4.4 Location map for Site D, Fourteenth Avenue, Rouge River basin

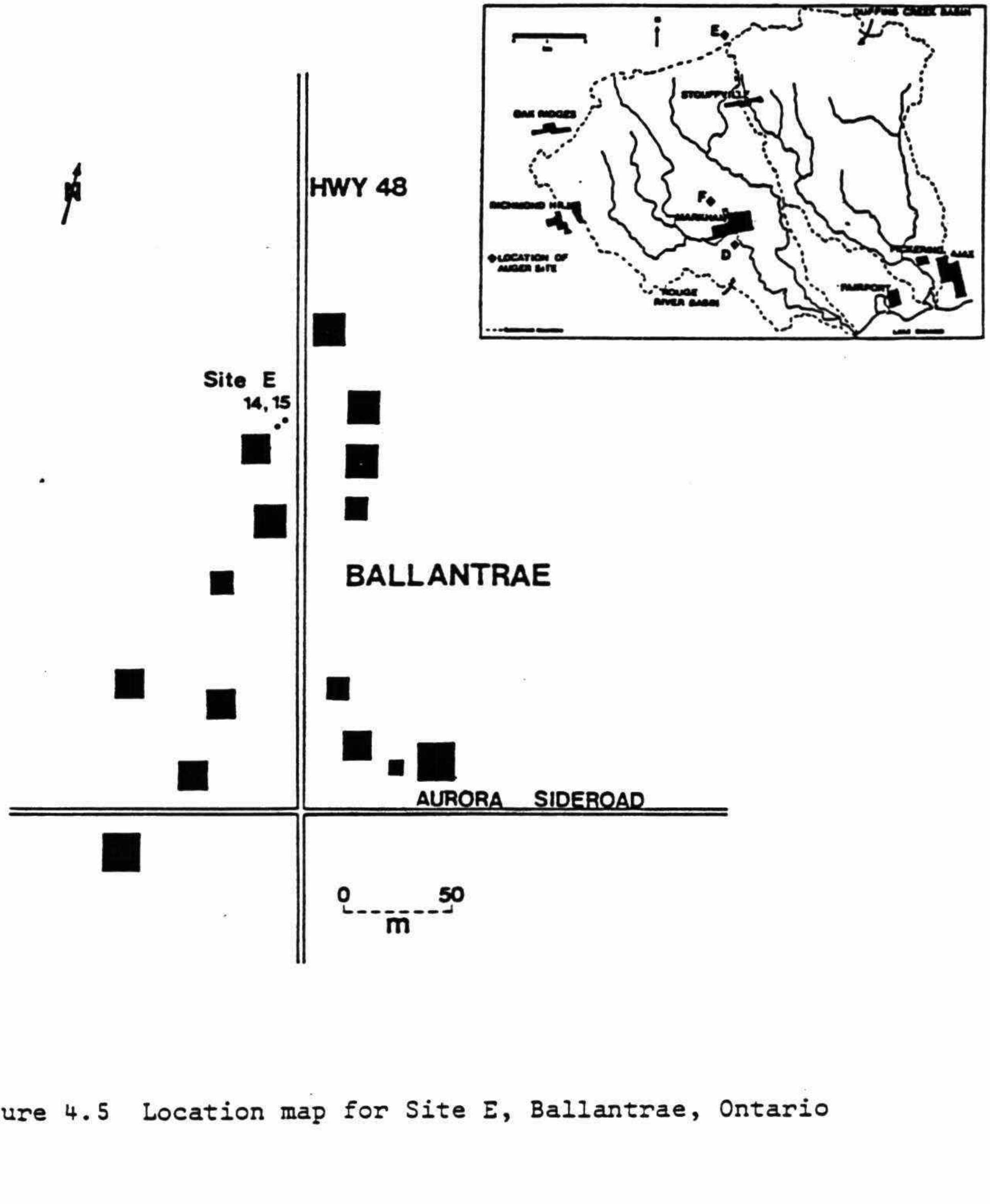


Figure 4.5 Location map for Site E, Ballantrae, Ontario

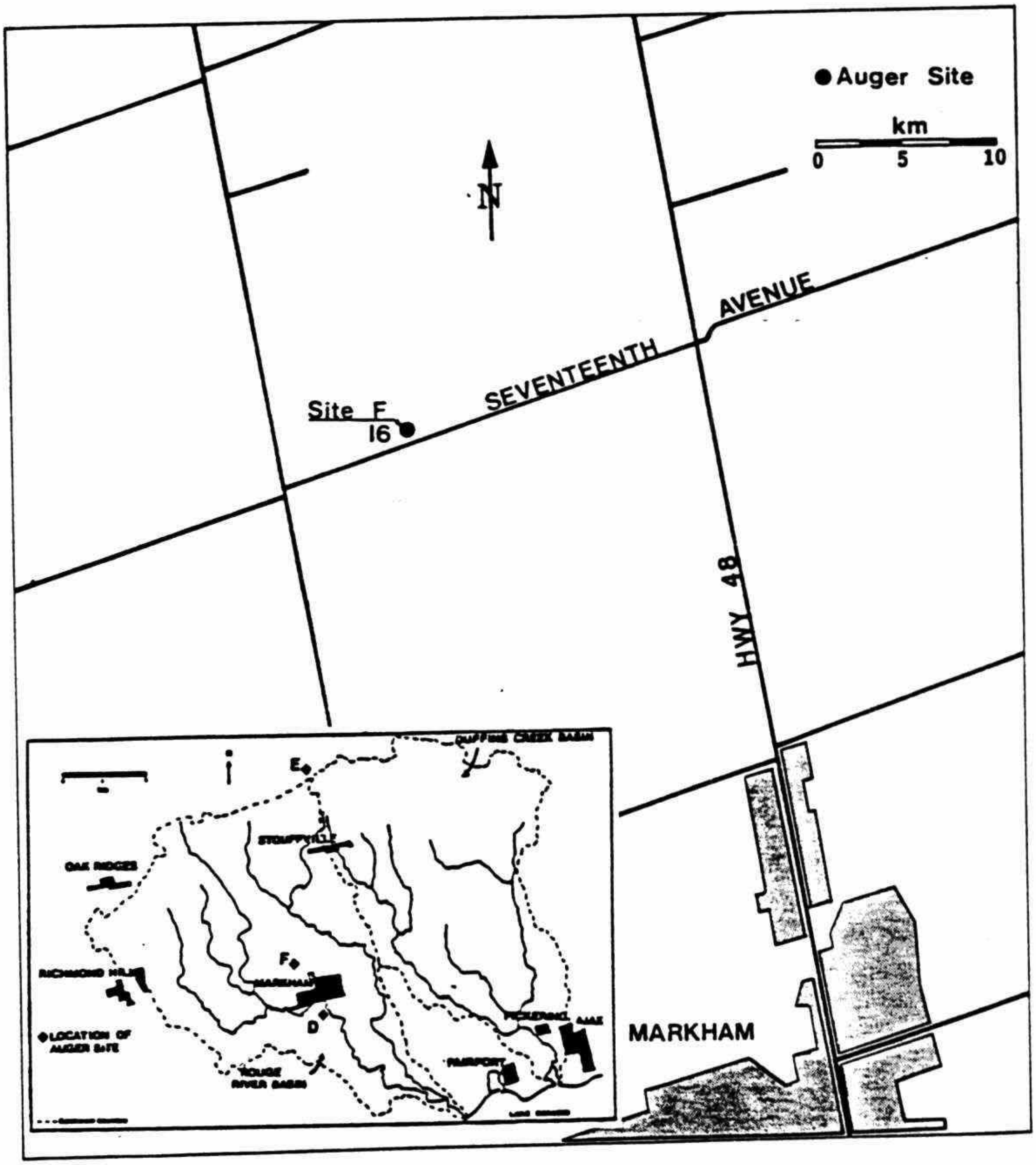


FIGURE 4.6 Location map for Site F, in a cornfield north of Markham, Ontario

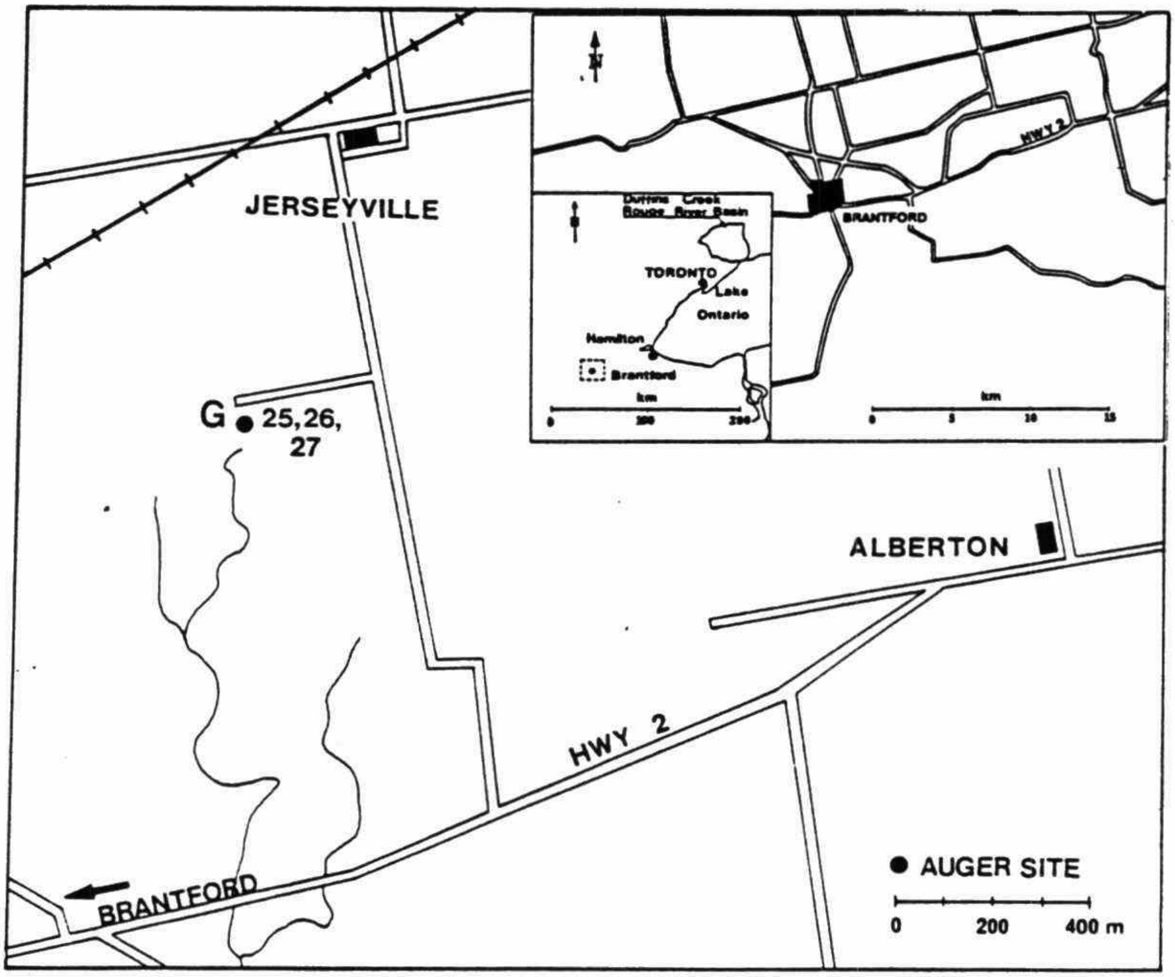


FIGURE 4.7 Location map for Site G, in a cornfield east of Brantford, Ontario

Research conducted by Barber et al. (1977) indicates that the chemical composition of the interstitial water can change under warm conditions, and that samples are least affected by storage if refrigerated or frozen. For this reason the sediment samples were refrigerated or frozen on their arrival at the laboratory.

Interstitial water was extracted from the sediment samples as soon as possible (usually beginning the same day as collection) so as to minimise the risk of chemical alteration of the interstitial water (Barber et al., 1977). Approximately 150 to 200 g of sediment was placed in specially designed Delrin centrifuge cups (Figure 4.8). These cups cup consist of an upper cylindrical portion into which the sediment sample is placed, separated from a lower detachable base into which the water passes during centrifugation. The material is supported by a Delrin base-plate covered with a Whatman No. 4 filter paper. Sediment samples were centrifuged for 30 to 60 minutes at a speed of 2500 to 3500 rpm and a temperature of 4° C. Clearly, the volume of interstitial water collected will depend on the period of centrifugation, quantity of sample, pore size distribution of the material, the degree of initial saturation, and the centrifuge dimensions (Edmunds et al., 1976). Typically, the sandy loam of the Don Valley and the Markham clay sampled in the Rouge River yielded between 100 to 350 ml and 10 to 75 ml of interstitial water respectively.

The interstitial pore waters were analysed for as many chemical parameters as possible, given the volume of water available. To obtain geochemical data on the sediments, a total of thirty-five soil samples were submitted for instrumental neutron activation analysis as described in Appendix I.

4.3 Quality Control

4.3.1 Introduction

An analytical quality control program is necessary to produce reliable laboratory data. This program should ideally consist of three parts; 1) utilizing analytical techniques which have been found acceptable by laboratories collaboratively; 2) analyzing control samples regularly; and 3) analyzing reference samples.

This section discusses the quality control program adopted for the study. It considers the quality control measures as applied to each of the four stages of the data collection process: 1) sample collection (section 4.3.2); 2) sample preparation (section 4.3.3); 3) sample analysis (section 4.3.4); and 4) data analysis (section 4.3.5).

4.3.2. Sample collection

As discussed in section 4.2.1.2, nalgene bottles were cleaned with 10% nitric acid and thoroughly rinsed with distilled water prior to collection of well water samples. To determine whether any of the nitric acid was retained by

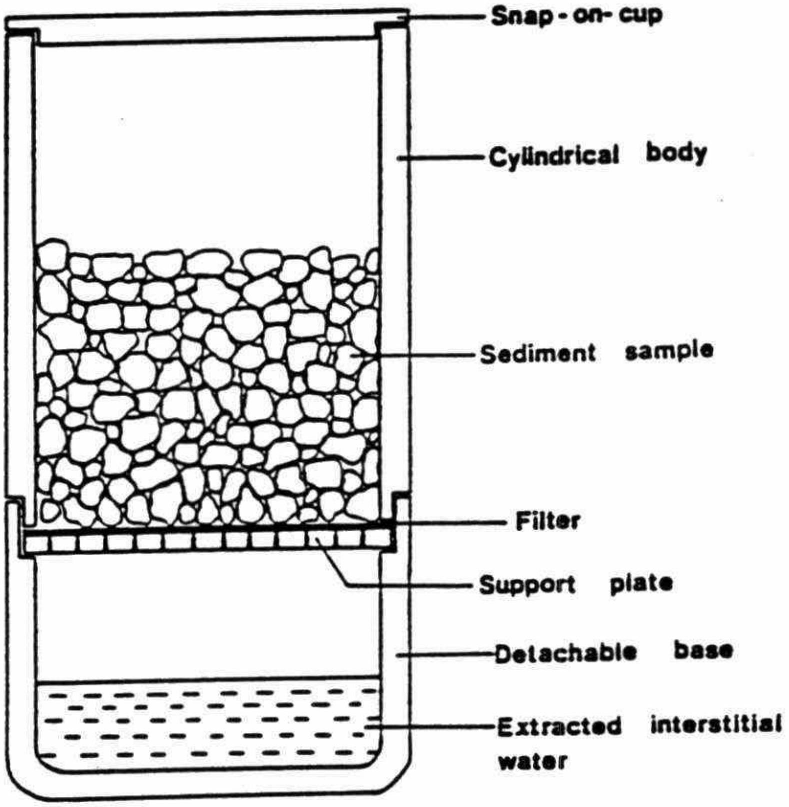


Figure 4.8 Section of centrifuge cup for interstitial water extraction

the bottle during this procedure, and was therefore contaminating the samples, a random selection of sample bottles were filled with double distilled water and allowed to soak for several days. The nitrate concentration of the water sample was then measured using potentiometry. No traces of nitrate were found.

To monitor potential contamination of groundwater samples during sample collection and filtering in the field, several blanks were processed using routine sample preparation procedures. Results of analyses of the blanks showed concentrations below determination limits for all parameters, with the exception of iron which varied from 0.6 to 1.0 mg/L. This problem was eliminated by the replacement of the automatic pipette used to acidify the samples for ICP-AES analysis with a standard volumetric pipette.

For the interstitial water samples, several measures were taken to ensure quality control. One measure involved the removal of the outer 2 cm of each sediment sample to avoid the risk of sample contamination by the metal body of the auger. In addition, two blanks were prepared to determine how contamination from the auger might affect water chemistry. These blanks were prepared by rinsing the auger with double distilled water, and submitting the samples for ICP-AES analysis. Results indicated that only barium concentrations were above ICP determination limits and were occasionally as high as 1.0 mg/L. The source of the barium is uncertain but may be derived from paint on the auger.

As discussed in section 4.2.3.2., interstitial water samples were collected from sediment samples using centrifugation. Potential contamination of interstitial water samples from the centrifuge cups used during the extraction of the sample was not investigated during this study. However, previous work has shown contamination during centrifugation to be negligible.

4.3.3. Sample preparation

To identify and control the possible contamination of samples by filtering and preconcentration procedures used in the laboratory, blanks of double distilled water were prepared for each set of samples analyzed. These blanks were filtered, acidified and pre-concentrated in the same manner as indicated in section 4.2. The values of the blanks were used to make corrections to the sample data where necessary.

4.3.4 Sample analysis

As a control on the quality of the major and minor ion analyses conducted in the Groundwater Research Laboratory, blanks of double distilled water were analyzed with each set of samples.

To determine the reliability of major and minor ion analysis, ten replicate samples were analyzed. Precision calculations were made for the 13 ions analyzed and are given in Appendix I.

For trace element analysis, National Bureau of Standards (NBS) water samples were analyzed on ICP along with every set of samples submitted. These standards are prepared by the National Bureau of Standards in the United States and contain 18 elements that have been measured by at least two or three acceptable analytical techniques. The NBS samples were used to determine precision and accuracy for element measured.

4.3.5 Data analysis

To provide a check on the quality of the major ion chemical analyses, anion-cation balances were performed on all samples with a complete suite of major ion analyses. The formula for this calculation is

$$\text{Error} = (\text{cations} - \text{anions}) / (\text{cations} + \text{anions})$$

Samples having errors of 10% were reanalyzed and if the error could not be corrected they were not used.

For neutron activation analyses, samples with analytical errors of 30% or more were not used in the the interpretation. To determine the error for each sample the following formula was used:

$$\text{Error} = (\text{count} - \text{background}) / (\text{count} + \text{background})$$

5. RESULTS AND INTERPRETATION

5.1 Introduction

This section presents and discusses the results of the hydrochemical investigation. It is divided into three parts, each part corresponding to the three objectives outlined in Section 1.

The first major section (Section 5.2) concerns the concentrations of major, minor, and trace chemical constituents of groundwaters of the Duffins Creek-Rouge River basins. It provides a rigorous understanding of the background chemistry of the region, and draws attention to anomalies which may be indicative of groundwater contamination.

The following section (Section 5.3) examines the potential source contaminants and characterizes them on the basis of their chemical composition. For this part of the study emphasis was placed on five principal chloride enriching contaminants; road de-icing chemicals, inorganic and organic fertilizers, sewage sludges, landfill leachates and bedrock waters.

The next section (Section 5.4) discusses the results of the interstitial water sampling program, the purpose of which was to confirm that non-point source contaminants are accumulating in the shallow sub-surface, and to develop, through a knowledge of their sub-surface chemical character, a convenient and definitive hydrochemical method of identifying the contaminant origins.

Section 5 concludes with a summary (Section 5.4) which discusses the relationship between the chemical character of the potential contaminants and the chemical character of the interstitial waters.

5.2 Groundwaters

The classification system developed by Beck (1985) was based on the major and minor ion analyses of a large suite (approximately 260) of groundwater samples. The current study comprised a smaller suite of groundwaters, resampled from sites chosen by Beck (1985), but included trace element analysis in addition to major and minor ion analysis. The samples were restricted to overburden wells and were selected so as to provide representation of the various water types identified by Beck. At the same time an attempt was made to provide regional coverage of the Duffins Creek - Rouge River drainage basins. A full description of the sites is contained in Appendix E of Beck (1985). Clearly, an important first stage of this new study was to demonstrate that the major ion classification scheme used by Beck (1985) and later modified by Howard and Beck (1986) was still appropriate to the region and that no major changes had occurred to the hydrochemical flow regime.

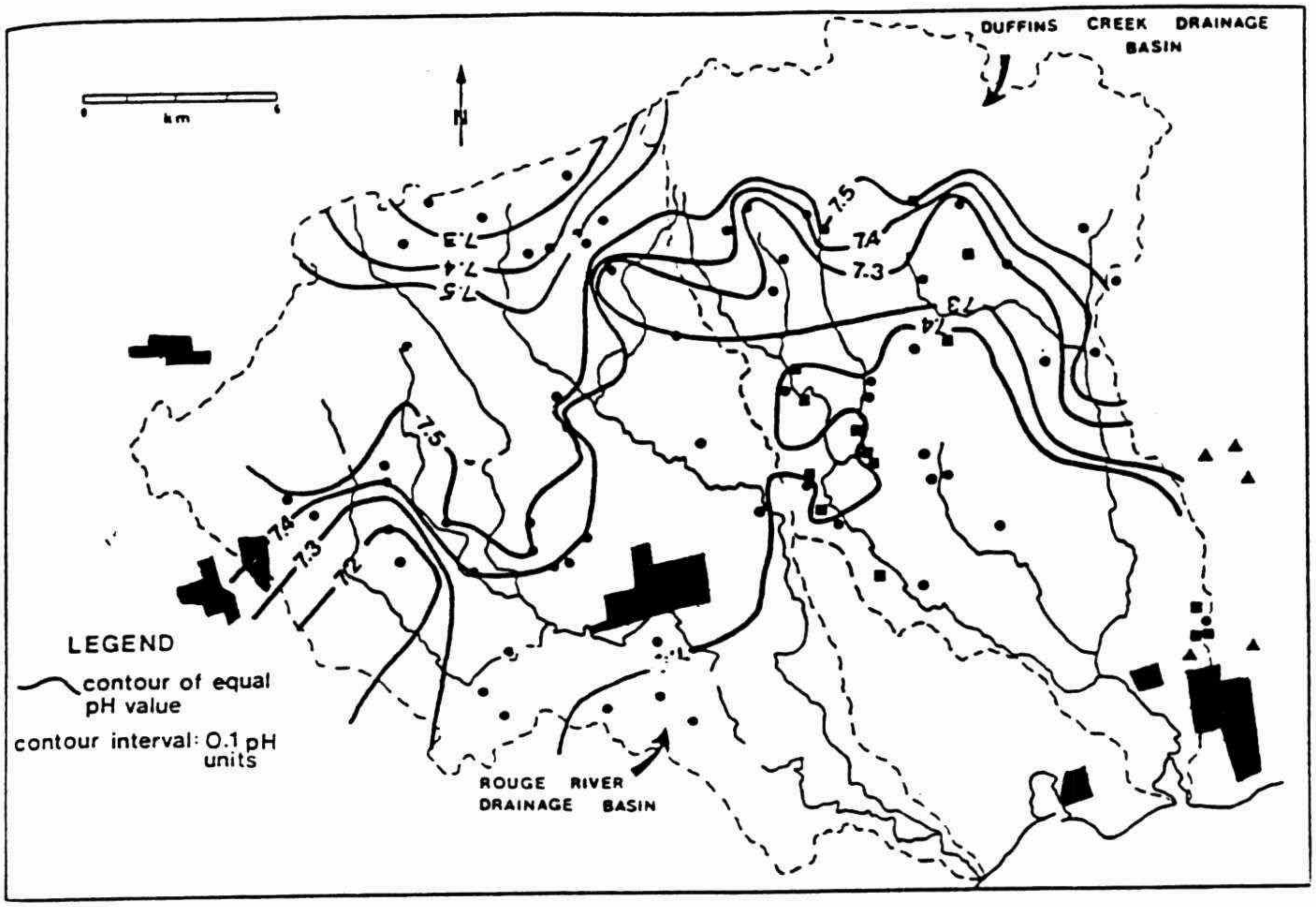

DUFFINS CREEK DRAINAGE BASIN
km
0
6
N
7.5
7.4
7.3
7.5
7.4
7.3
7.2
LEGEND
contour of equal pH value
contour interval: 0.1 pH units
ROUGE RIVER DRAINAGE BASIN

Figure 5.1a Distribution of pH

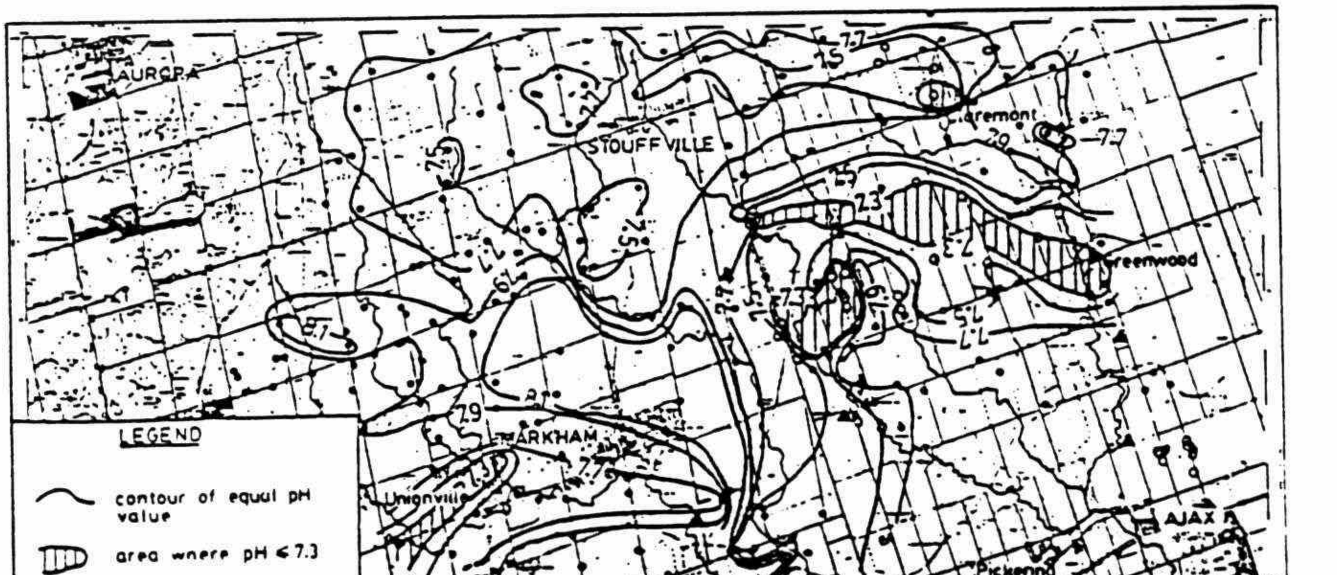


Figure 5.1b Distribution of pH (Beck, 1985)

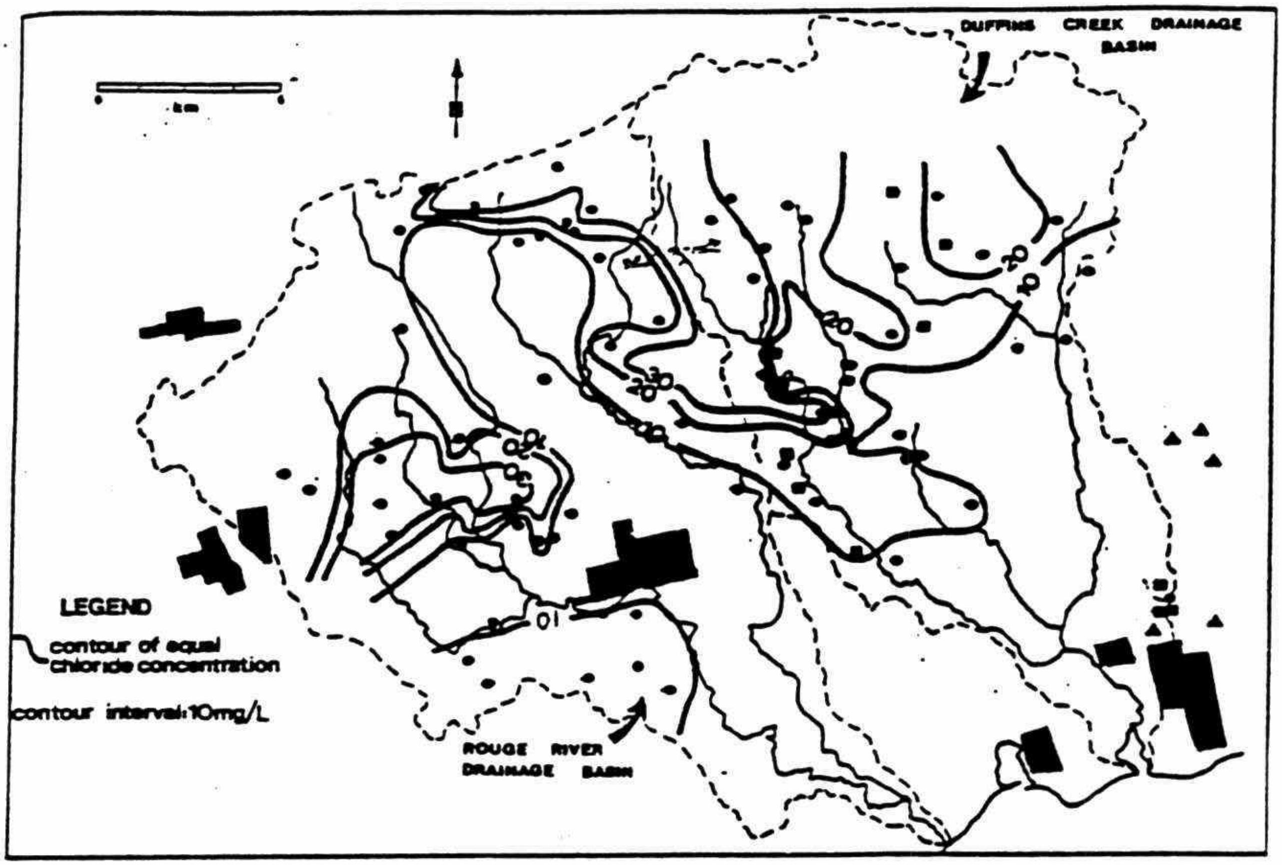

DUFFINS CREEK DRAINAGE BASIN
0
km
6
10
20
30
LEGEND
contour of equal chloride concentration
contour interval:10mg/L
ROUGE RIVER DRAINAGE BASIN

Figure 5.2a Distribution of chloride

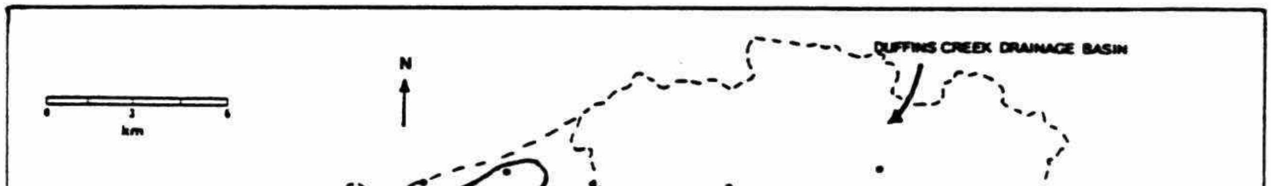


Figure 5.2b Distribution of chloride (Howard, 1985)

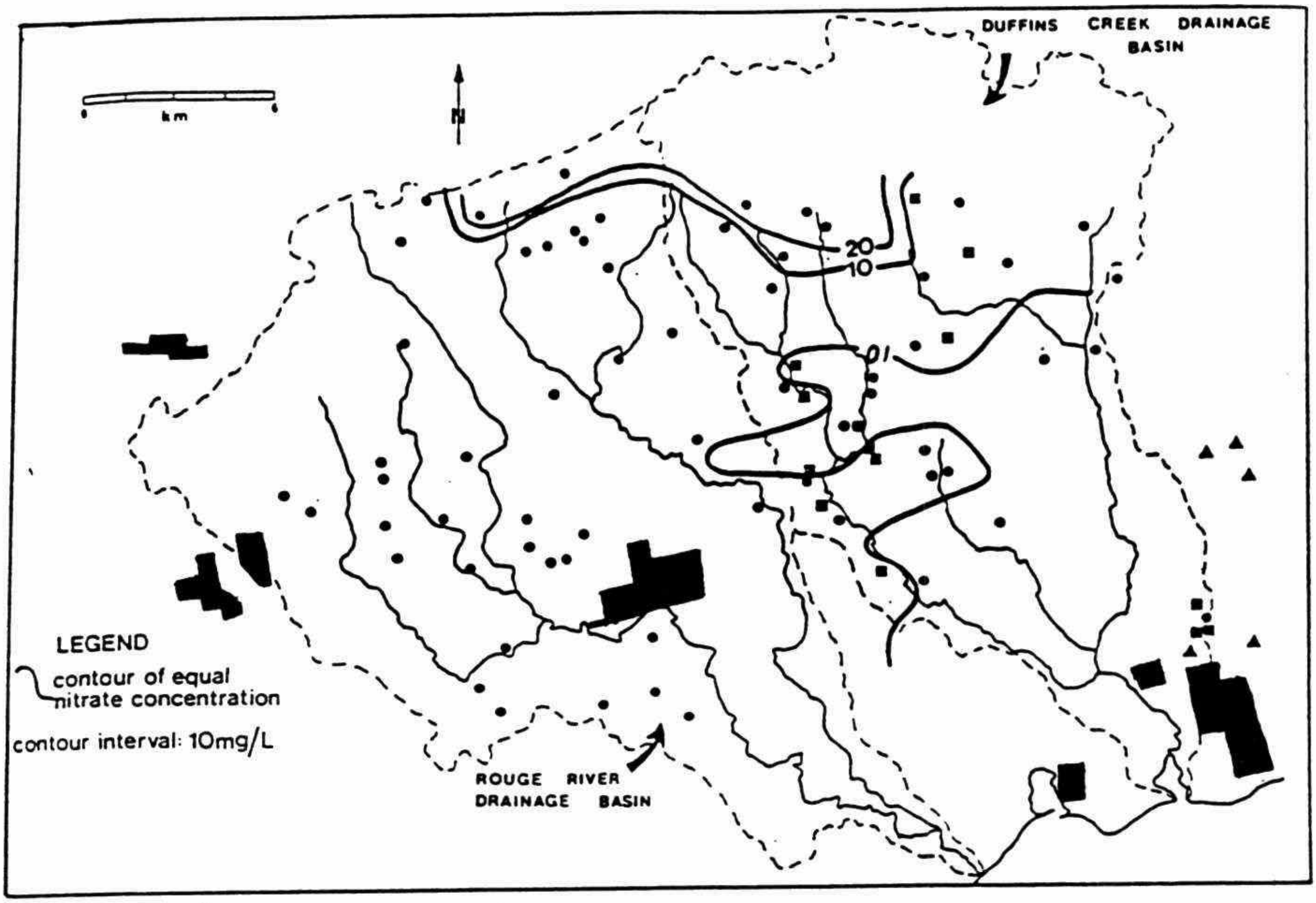

DUFFINS CREEK DRAINAGE BASIN
0
km
6
N
20
10
10
LEGEND
contour of equal nitrate concentration
contour interval: 10mg/L
ROUGE RIVER DRAINAGE BASIN

Figure 5.3a Distribution of nitrate

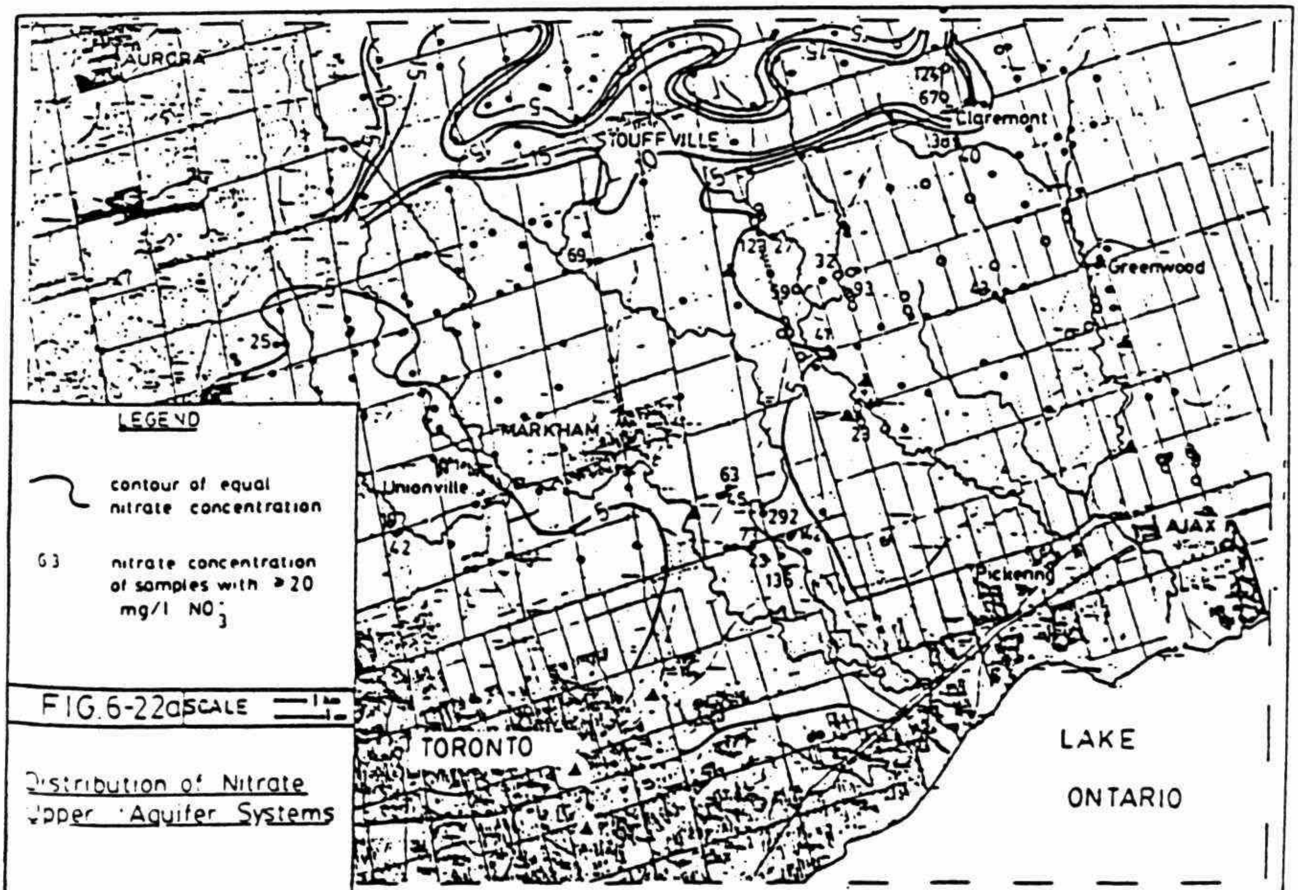


Figure 5.3b Distribution of nitrate (Beck, 1985)

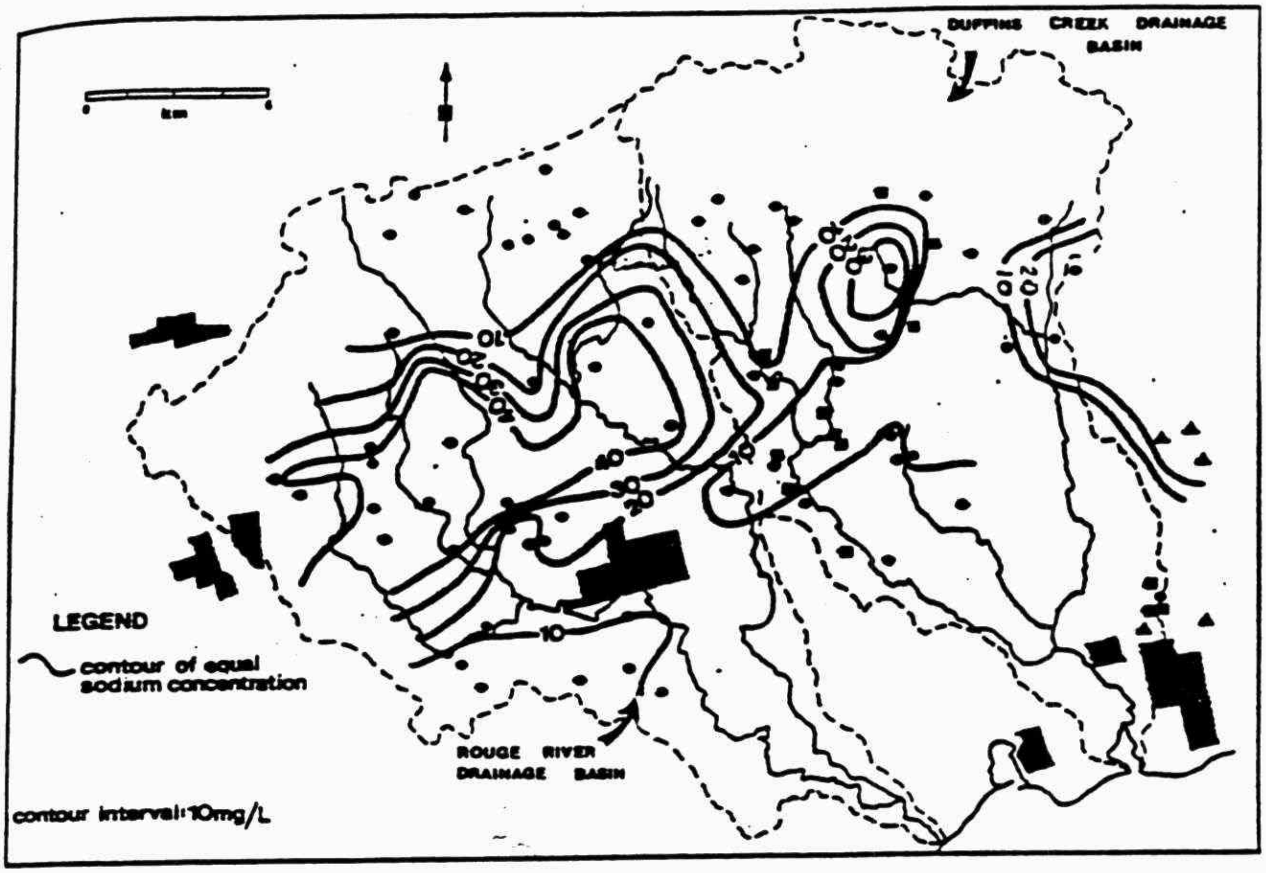

DUFFINS CREEK DRAINAGE BASIN
km
LEGEND
contour of equal sodium concentration
ROUGE RIVER DRAINAGE BASIN
contour interval:10mg/L
10
20
30
40

Figure 5.4a Distribution of sodium

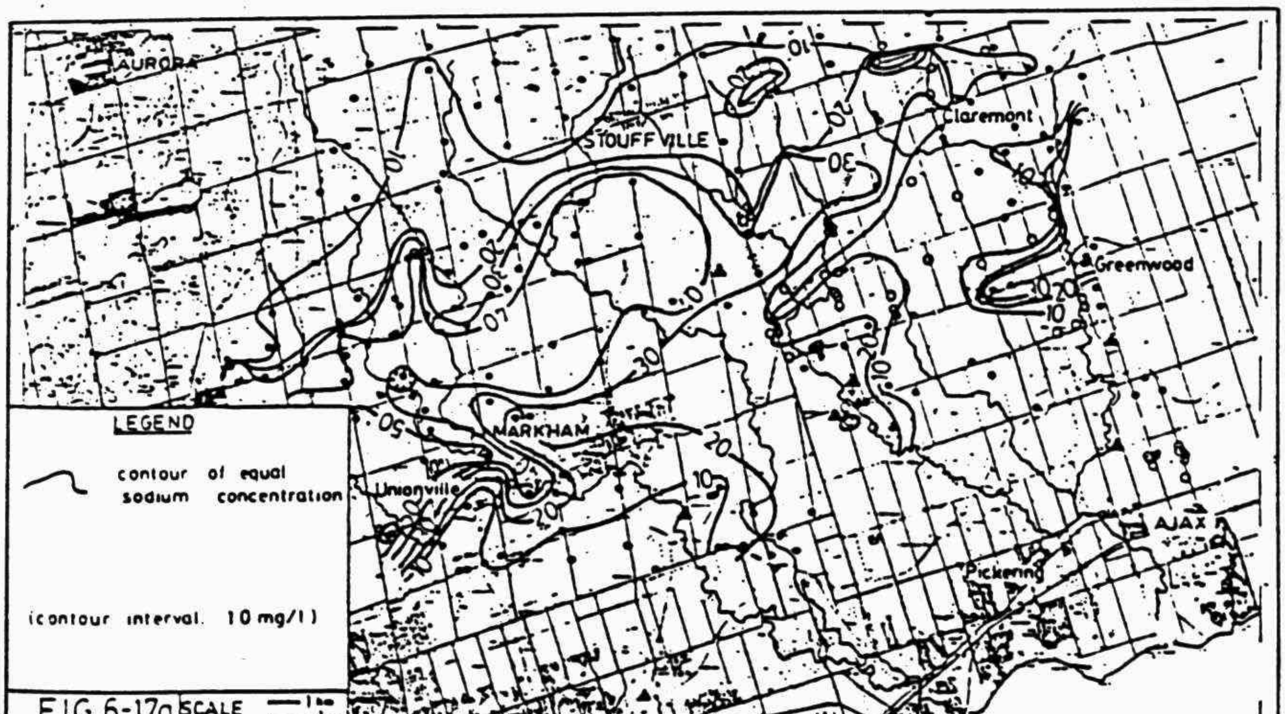


Figure 5.4b Distribution of sodium (Beck, 1985)

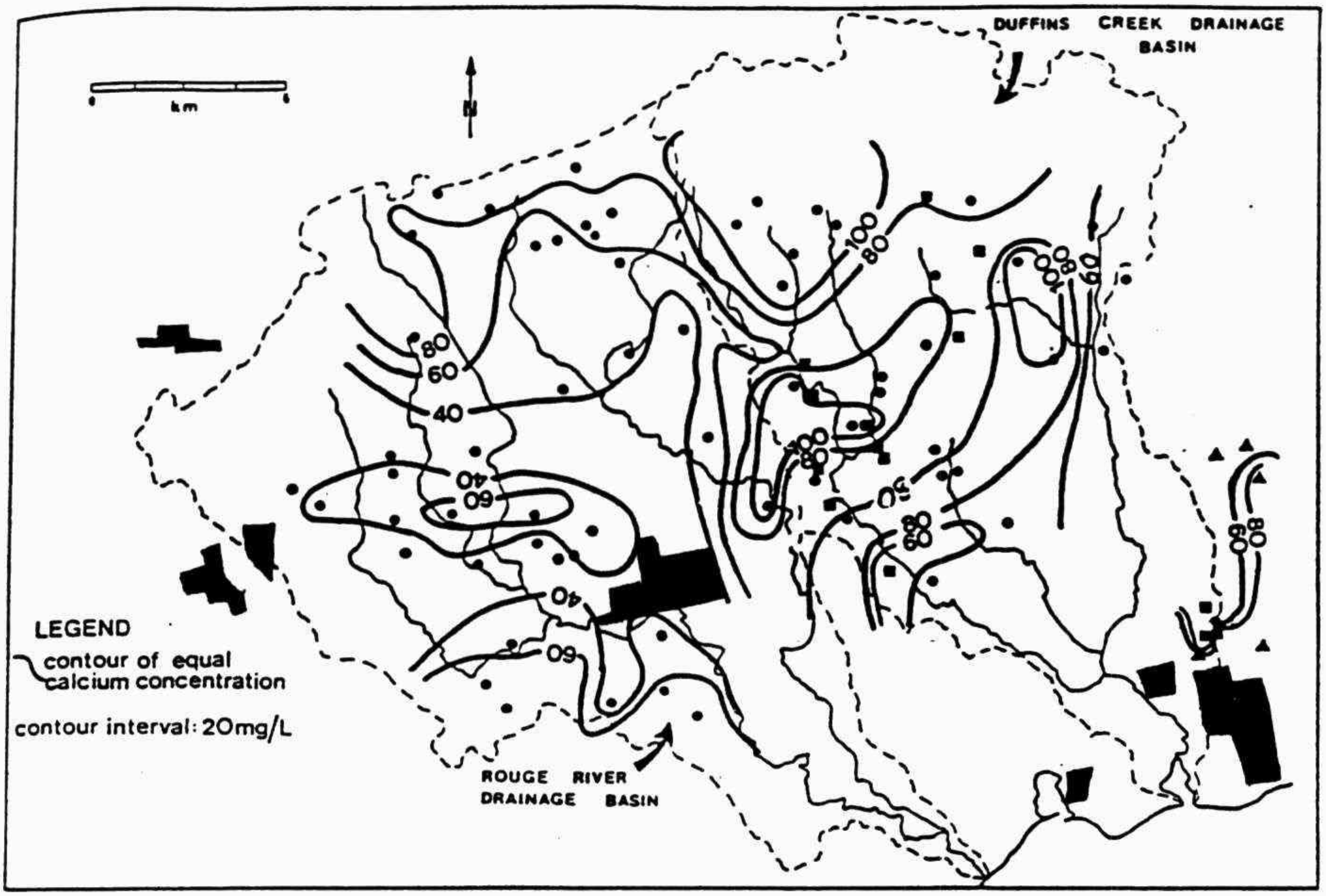

DUFFINS CREEK DRAINAGE BASIN
km
N
100
80
60
40
LEGEND
contour of equal calcium concentration
contour interval: 20mg/L
ROUGE RIVER DRAINAGE BASIN

Figure 5.5a Distribution of calcium

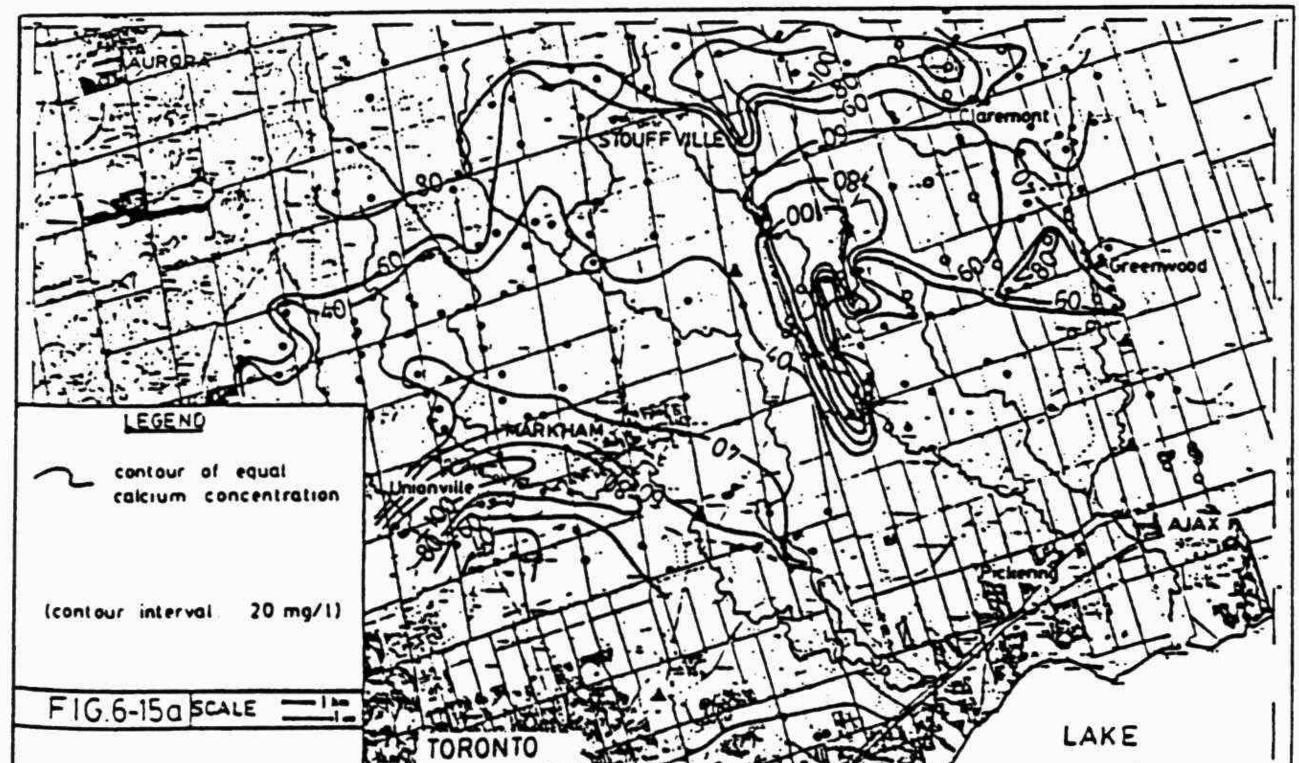


Figure 5.5b Distribution of calcium (Beck, 1985)

5.2.1 Regional distribution of major and minor ion parameters

To aid in the groundwater classification, a comparison was made between the distributions of major and minor ion parameters measured in this study and the distributions of the same parameters mapped by Beck (1985). Chemical distributions relevant to the discussion are presented in Figures 5.1a, 5.2a, 5.3a, 5.4a, 5.5a which show the 1986 regional distribution of pH, Cl, NO_3, Na, Ca respectively, and Figures 5.1b, 5.2b, 5.3b, 5.4b, and 5.5b which show the regional distribution of these parameters as mapped by Beck (1985). Other chemical distributions are presented in Appendix VI.

A direct comparison is difficult as the current study was based on a much smaller distribution of sample sites. Also it must be recognized that the water chemistry at most sites will exhibit some degree of temporal variability. Nevertheless, several parameters show important similarities. For example, both studies confirm that chloride concentrations are highest in the northern part of the Duffins Creek drainage basin, and to the north and west of Markham in the Rouge River drainage basin (Figures 5.2a and 5.2b). Similarly, highest nitrate concentrations occur in the extreme north of the area (Figures 5.3a and 5.3b) with sporadic high values (>10 mg/L) several kilometres south east of Stouffville.

Probably most significant is the similarity in sodium and calcium concentrations. Sodium concentrations, as previously shown by Beck (1985), tend to exhibit an inverse distribution to that of calcium (Figures 5.4a and 5.5a). In the Duffins Creek basin, sodium concentrations are low (< 10 mg/L) while calcium concentrations are commonly 60-100 mg/L. In the central part of the Rouge River drainage basin, calcium concentrations are generally low (<60 mg/L), while sodium concentrations are high (> 30 mg/L). The inverse relationship between Na and Ca was interpreted by Beck (1985) as indicative of ion exchange between Na and Ca. Groundwaters in recharge areas tend to exhibit low Na and high Ca; as groundwaters move through the system Ca is replaced by Na. It was evidence of this type which led Beck to conclude that recharge to the system occurred throughout most of the area but was impeded by Lake Markham clays in the central part of the Rouge drainage basin, immediately north of Markham.

5.2.2 Classification of groundwaters

5.2.2.1 Uncontaminated groundwaters

Of the 83 samples with complete major and minor ion analyses, 12 samples were classified as naturally evolving uncontaminated Type 1A, 2A, 3A and 4A groundwaters. These are represented on a modified form of the Durov diagram shown in Figure 5.6.

Type 1A uncontaminated recharge waters (Figure 5.6) plot in the top left hand corner of the diagram and are classified as calcium-bicarbonate ($Ca-HCO_3$) waters. Groundwaters which have undergone ion exchange as described in Section 3.2 are classified as Types 2A, 3A, or 4A depending on the degree to which ion

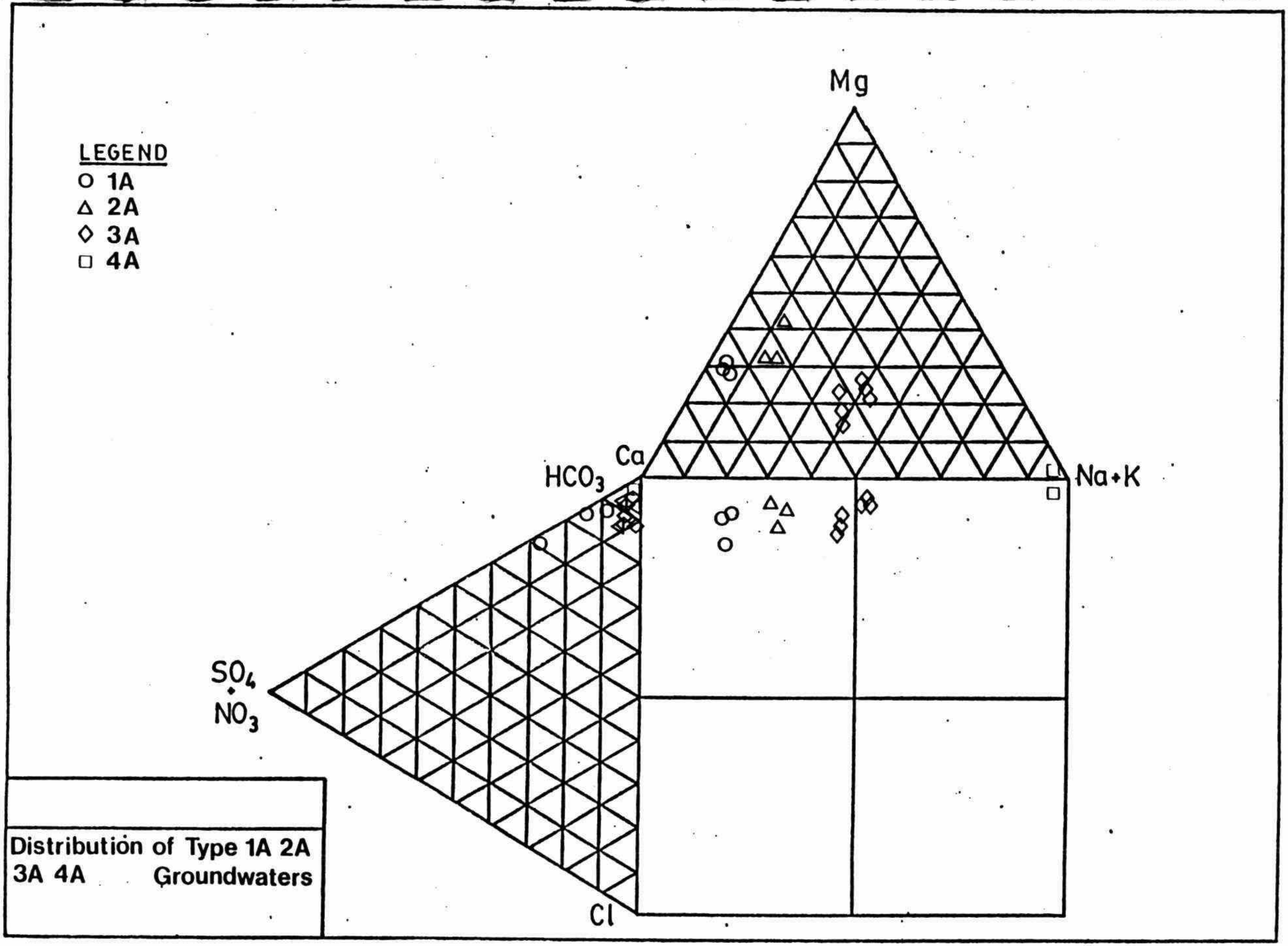


FIGURE 5.6 Distribution of Types 1A, 2A, 3A and 4A groundwaters

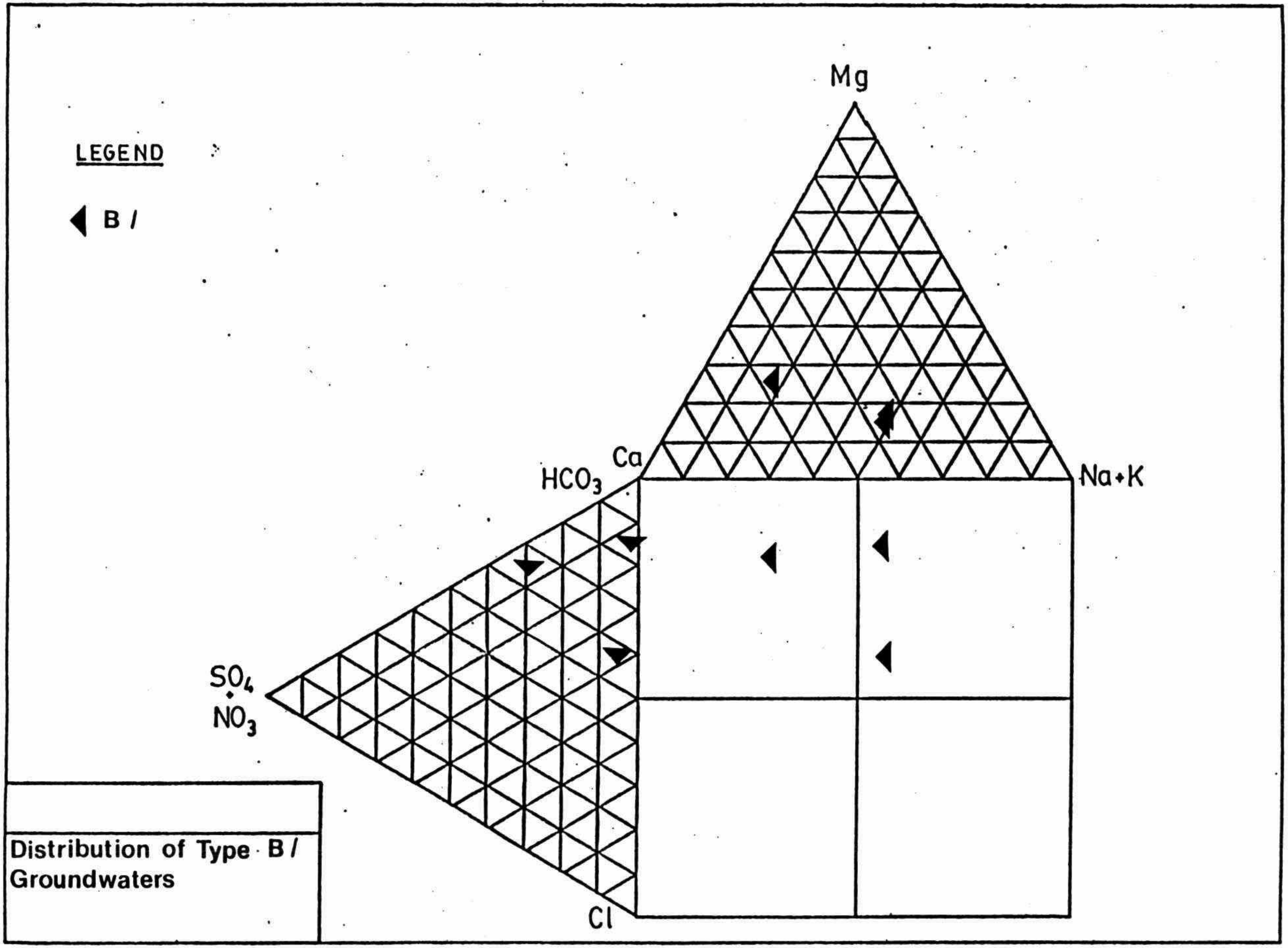


FIGURE 5.7 Distribution of Type B-1 bedrock waters

exchange has occurred. These waters plot in a band from the upper left hand corner of the $Ca-HCO_3$ field into the upper right hand corner of the $(Na+K)-HCO_3$ field (Figure 5.6).

Bedrock waters collected in the Pickering area were classified as Type B-1, sodium bicarbonate waters (Figure 5.7). The history of evolution of these waters is unknown and it is possible that they may be at least partly connate in origin.

5.2.2.2 Contaminated groundwaters

The remaining waters can be classified as contaminated, albeit perhaps to a minor extent. This classification is based on the work of Beck (1985) and Howard (1985) (see Table 3.1 (section 3.2)) which indicated that maximum background concentrations of chloride and nitrate in uncontaminated groundwaters of the Duffins Creek-Rouge River basins were approximately 15 mg/L and 10 mg/L (as nitrate) respectively.

Using the Howard and Beck (1986) classification scheme, the contaminated groundwaters can be grouped into one of 3 subtypes 1S, 1N, 1U depending on the speculated origins. Type 1S waters are enriched in chloride (see Table 3.1) and are thought to indicate contamination by NaCl road de-icing chemicals, while the elevated nitrate concentrations found in Type 1N waters are cautiously attributed to the application of fertilizers. The Type 1U classification is generally reserved for Type 1A recharge waters which contain elevated concentrations of both nitrate and chloride, and are therefore of indeterminate origin. In most cases, the contaminated waters are essentially calcium bicarbonate in character (i.e. Type 1A). However, in some cases older Type 2A through 4A waters become contaminated, in which case the resulting waters are classified as Types 2U, 3U, and 4U with no S or N designation.

Groundwaters classified as Types 1S and 1N are shown in Figure 5.8. Due to the elevated concentrations of chloride and nitrate in these waters they are generally displaced from the Type 1A field.

The remaining samples are classified as contaminated waters of undifferentiated origins (Types 1U through 4U) shown in Figure 5.9. Most of the undifferentiated contaminated groundwaters are Type 1A recharge waters which show enrichment in chloride and/or nitrate.

5.2.3 Distribution of groundwater Types

The distribution of the groundwater Types is shown in Figure 5.10a. This distribution is very similar to the distribution of chemical water types mapped by Beck (1985) and Beck and Howard (1985) (Figure 5.10b.) in 1984-85. The similarity of the distributions reinforces the conclusions of the previous studies and confirms that no major changes have occurred in the hydrochemical flow regime of the region.

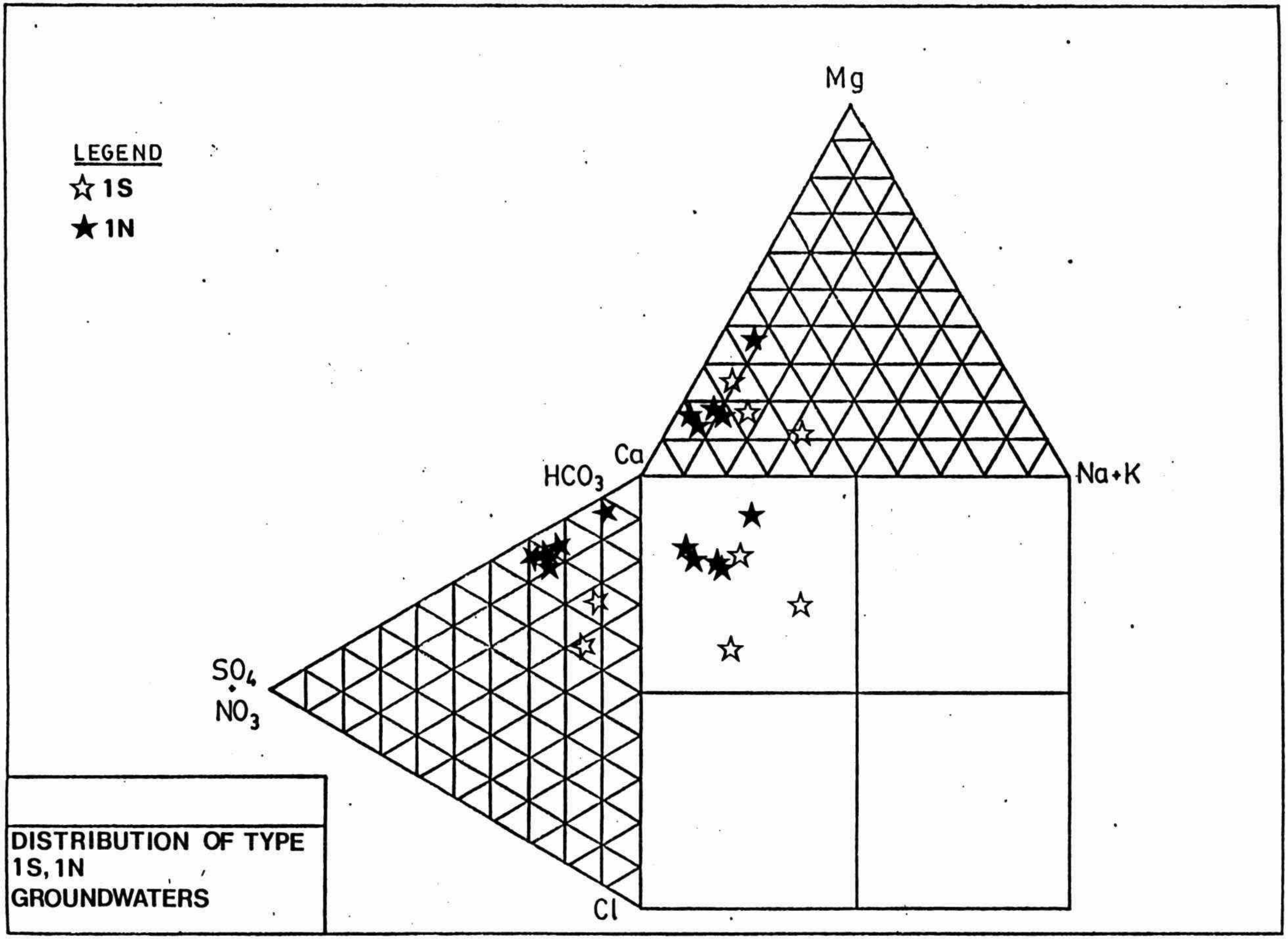


FIGURE 5.8 Distribution of Type 1S and 1N groundwaters

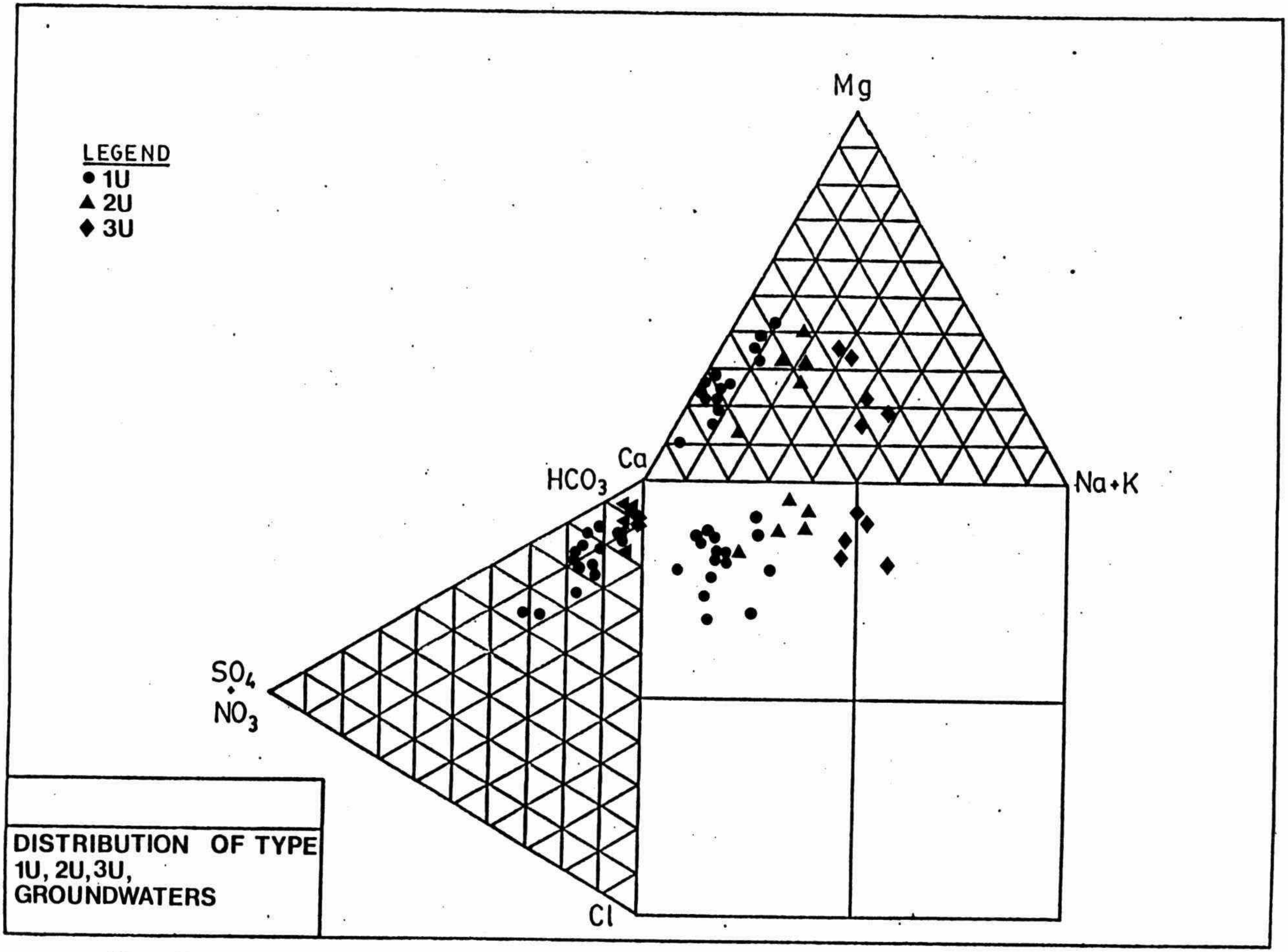


FIGURE 5.9 Distribution of Types 1U, 2U and 3U groundwaters

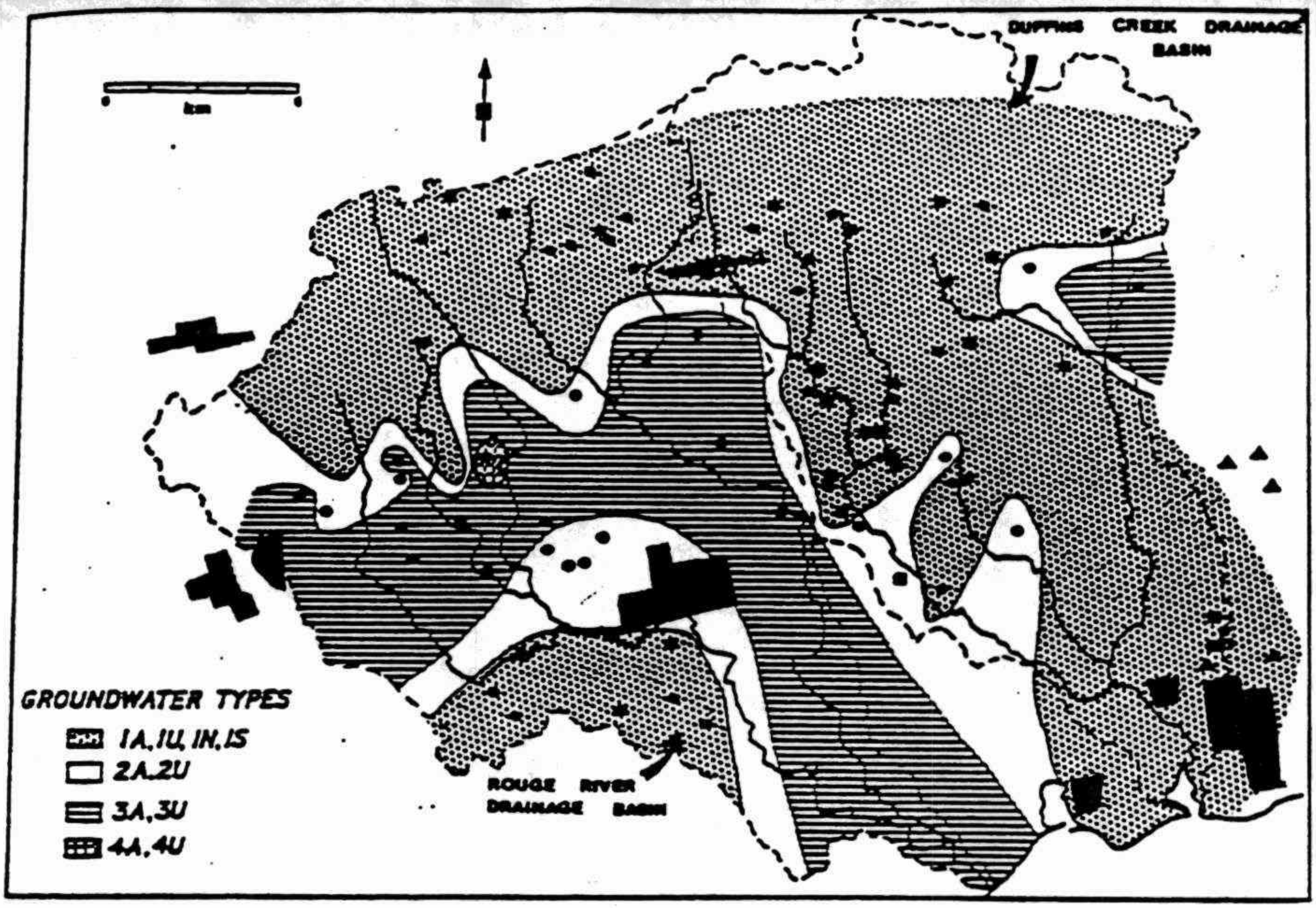


Figure 5.10a Distribution of groundwater types

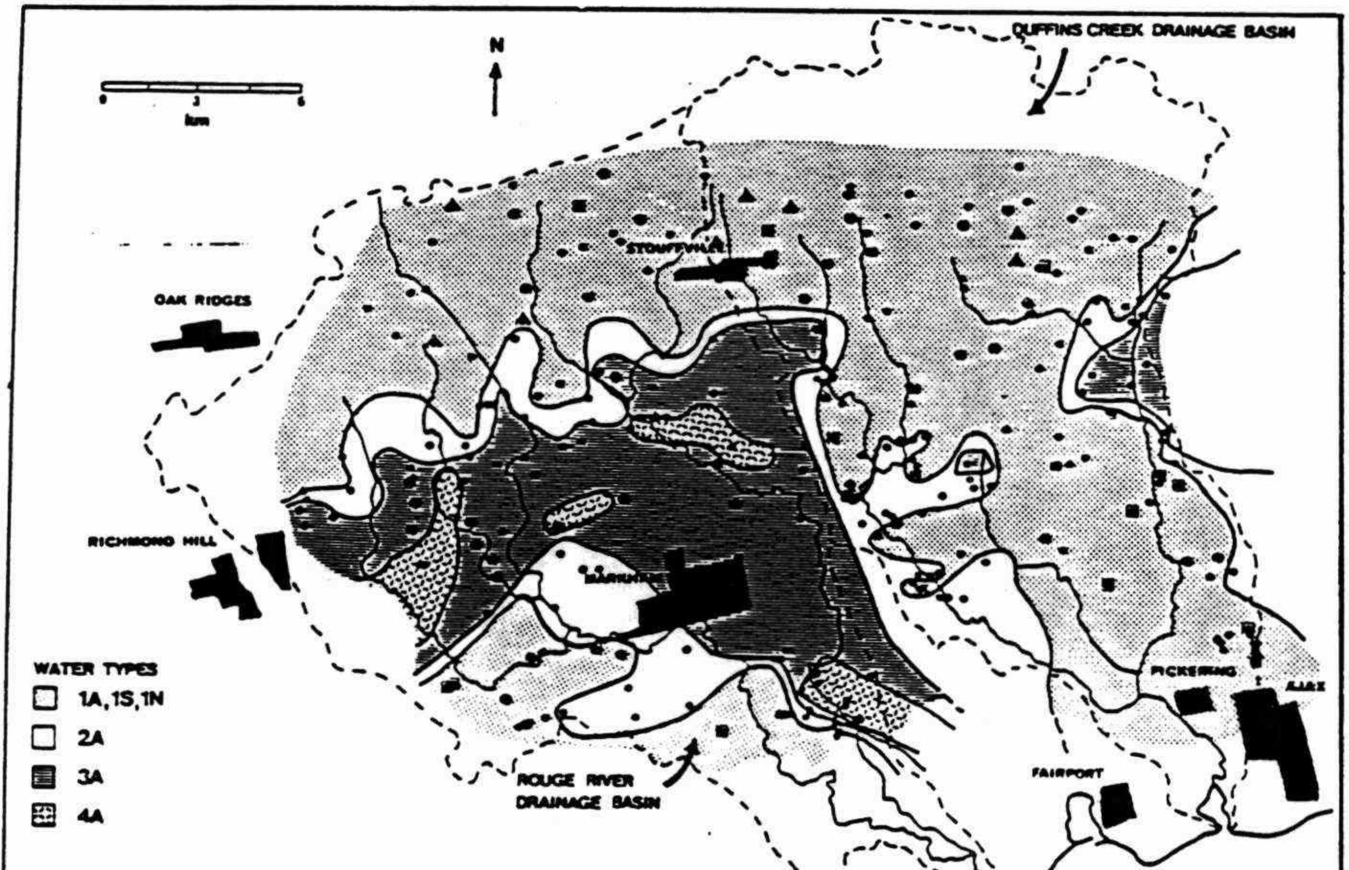


Figure 5.10b Distribution of groundwater types (Howard, 1985)

As shown in Figure 5.10a, Type 1 recharge waters (1A, 1S, 1N, 1U) occupy the northern part of the Rouge River basin (Oak Ridges area) which was identified by Beck (1985) as a primary region of groundwater recharge. Type 1 waters also occur in the area south of Unionville and Markham indicating recharge in this locality. Older, naturally evolving Type 2 through 4 groundwaters are located in the central part of the basin. Groundwater flow in the Duffins Creek basin is dominated throughout by Type 1 undifferentiated recharge waters. The presence of these waters indicates that recharge is occurring throughout much of the basin.

5.2.4. Distribution of minor and trace chemical constituents.

The water type classification shown in Table 3.1 was based primarily on major ion chemistry, and recognized the fact that groundwaters will undergo a natural chemical evolutionary change as they move through the system. Sometimes these evolutionary changes will be masked by contamination; for example the tendency for chloride to increase from < 5 mg/l in Type 1A waters to >15 mg/l in Type 4A waters is easily masked by minor amounts of contamination from a wide range of sources. Other evolutionary changes are more distinct, for example the process of Ca- Na exchange be recognized even when contamination is significant.

A knowledge of the natural evolutionary process is important, as it allows anomalies reflecting unnatural processes, such as contamination, to be recognized. It provides the baseline with which to compare the quality of other waters. Major ions are not the only groundwater parameters to be affected by chemical evolutionary processes. They are perhaps easiest to understand as they can be measured most reliably. However, since an objective of the study is to determine whether certain minor and trace chemical constituents may prove helpful in the recognition of contaminant origins, it is important that the background behaviour of these constituents also be established.

Distribution maps for manganese, barium, copper, iron, potassium, iodide, nickel and vanadium are shown in Figures 5.11 to 5.18 respectively. Maps for arsenic, antimony, phosphorous, zinc, boron and aluminum are contained in Figures VI.1 to VI.6 (Appendix VI).

The distribution maps reveal several interesting features. Most significant is the fact that most of the trace and minor chemical distributions were readily contoured in a form that, in a number of cases, matched well with the general distribution of water types shown in Figure 5.10a. The ease of contouring alone is remarkable when it is recognized that less than 10 % of the sampling points in the basin are free of contamination (i.e. Cl< 5 - 15 mg/L and NO_3 < 10 mg/L). Two important conclusions that can be drawn are i) distributions of many of the trace and minor chemicals are regionally controlled and show little sign of local influences, and ii) groundwater contamination has little influence on trace metal and minor ion chemistry.

In general, the minor ion and trace metal distributions fall into one of two groups; 1) those constituents whose distributions closely resemble the distribution of water types in the basins; and 2) those constituents which are

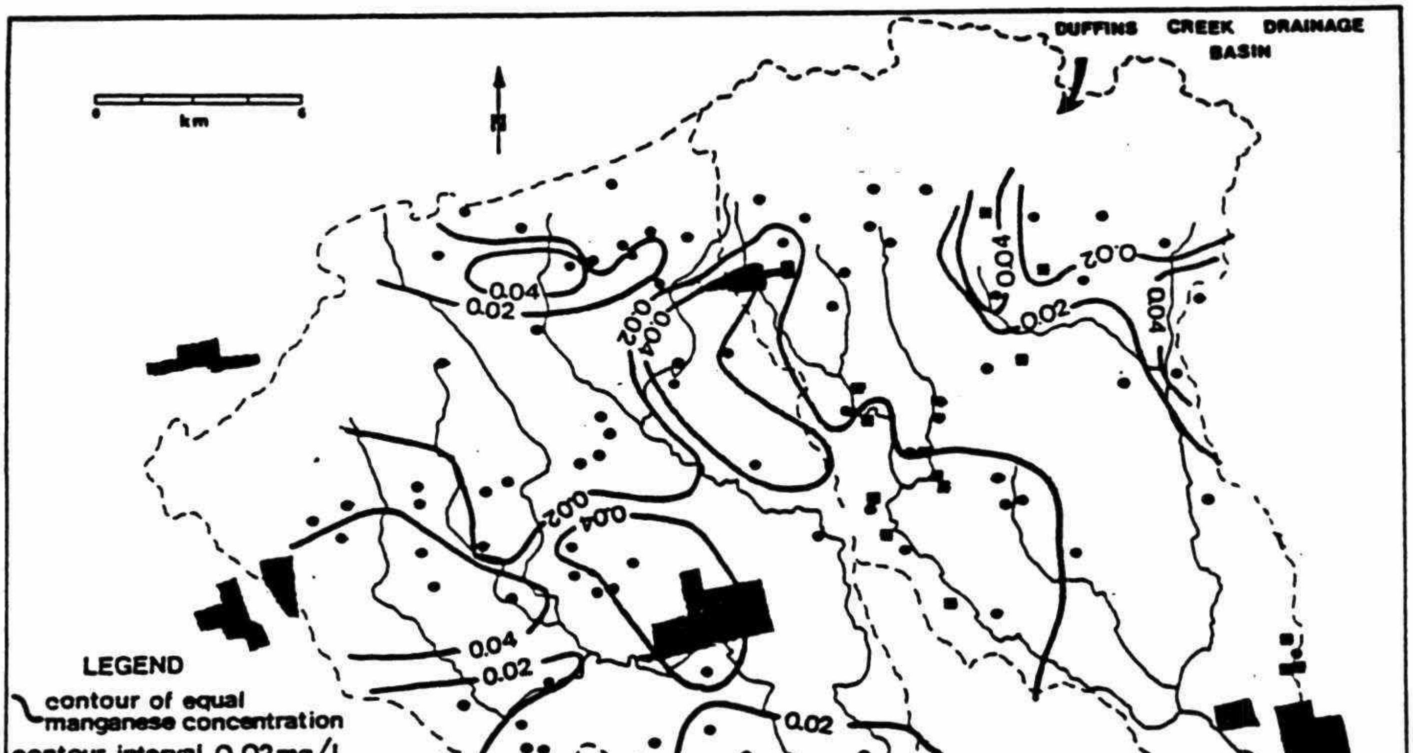

DUFFINS CREEK DRAINAGE BASIN
km
0
6
N
0.04
0.02
LEGEND
contour of equal manganese concentration
contour interval 0.02mg/L
ROUGE RIVER DRAINAGE BASIN

Figure 5.11 Distribution of manganese,Duffins Creek-Rouge River basins

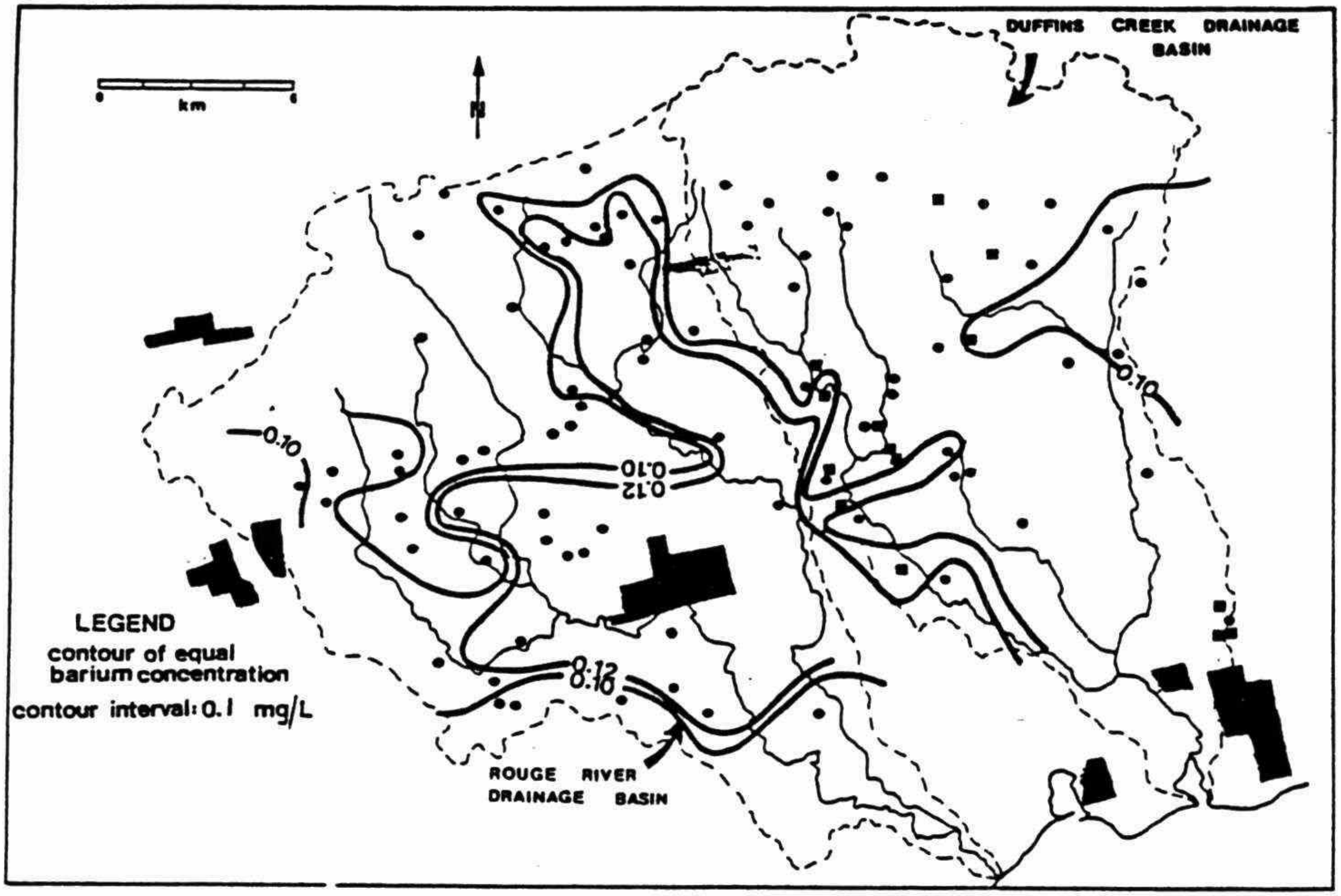

DUFFINS CREEK DRAINAGE BASIN
km
N
0.10
0.10
0.12
0.12
0.10
0.10
LEGEND
contour of equal barium concentration
contour interval: 0.1 mg/L
ROUGE RIVER DRAINAGE BASIN

Figure 5.12 Distribution of barium, Duffins Creek-Rouge River basins

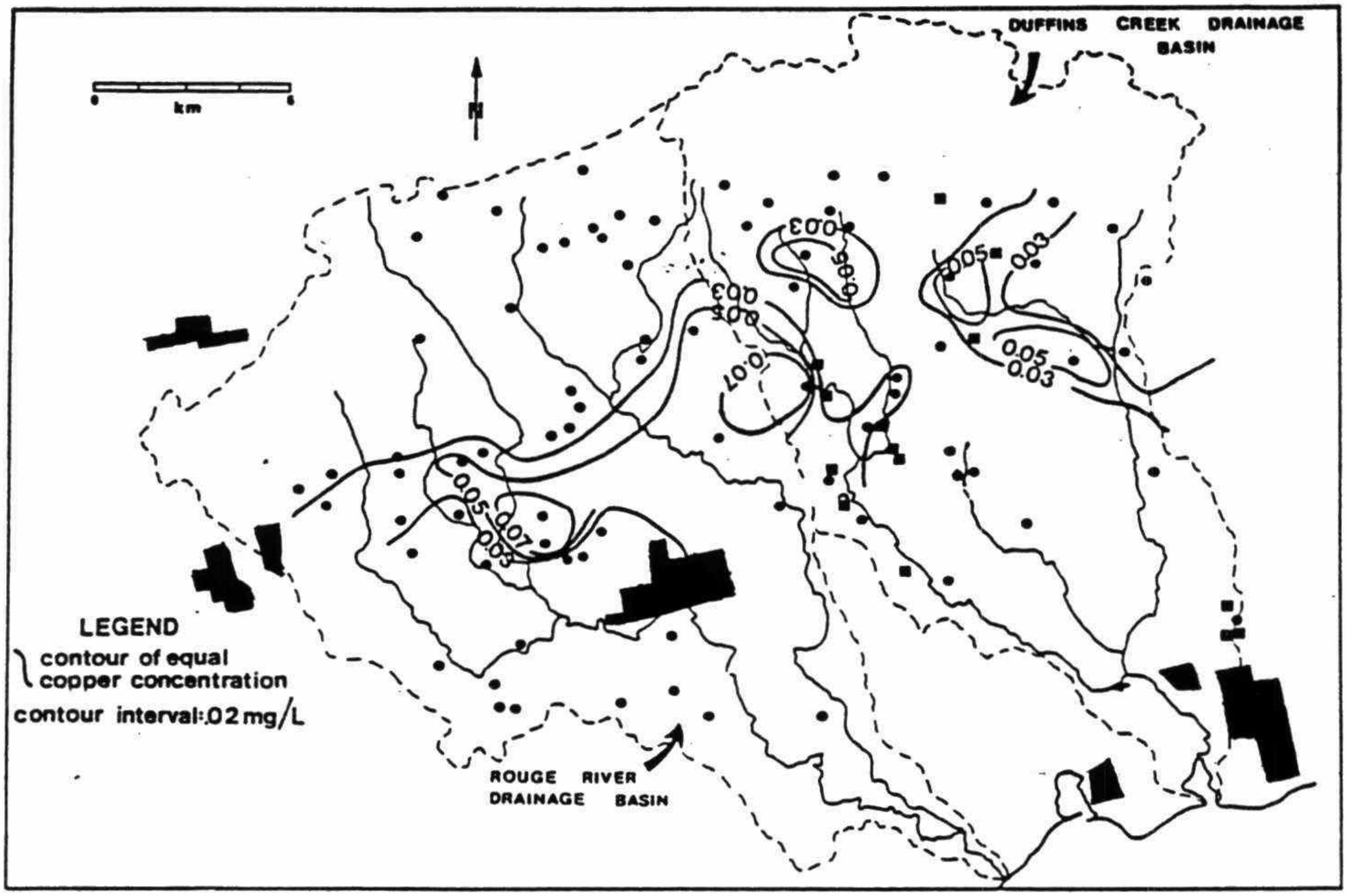

DUFFINS CREEK DRAINAGE BASIN
0
km
5
N
0.03
0.05
0.03
0.05
0.03
0.07
0.03
0.05
0.07
0.05
0.03
0.05
0.03
LEGEND
contour of equal copper concentration
contour interval:.02 mg/L
ROUGE RIVER DRAINAGE BASIN

Figure 5.13 Distribution of copper, Duffins Creek-Rouge River basins

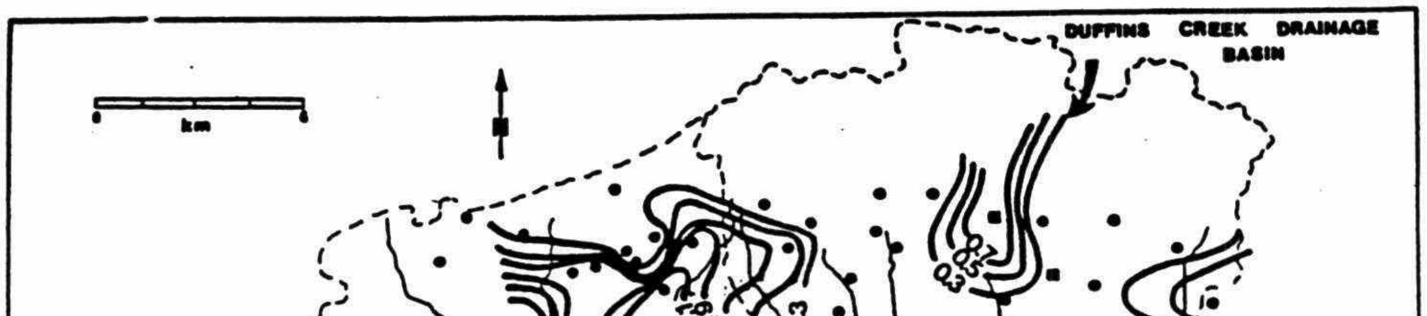

DUFFINS CREEK DRAINAGE BASIN
km
N
0.3
0.5
0.7
LEGEND
contour of equal iron concentration
contour interval 0.2mg/L
ROUGE RIVER DRAINAGE BASIN

Figure 5.14 Distribution of iron, Duffins Creek-Rouge River basins

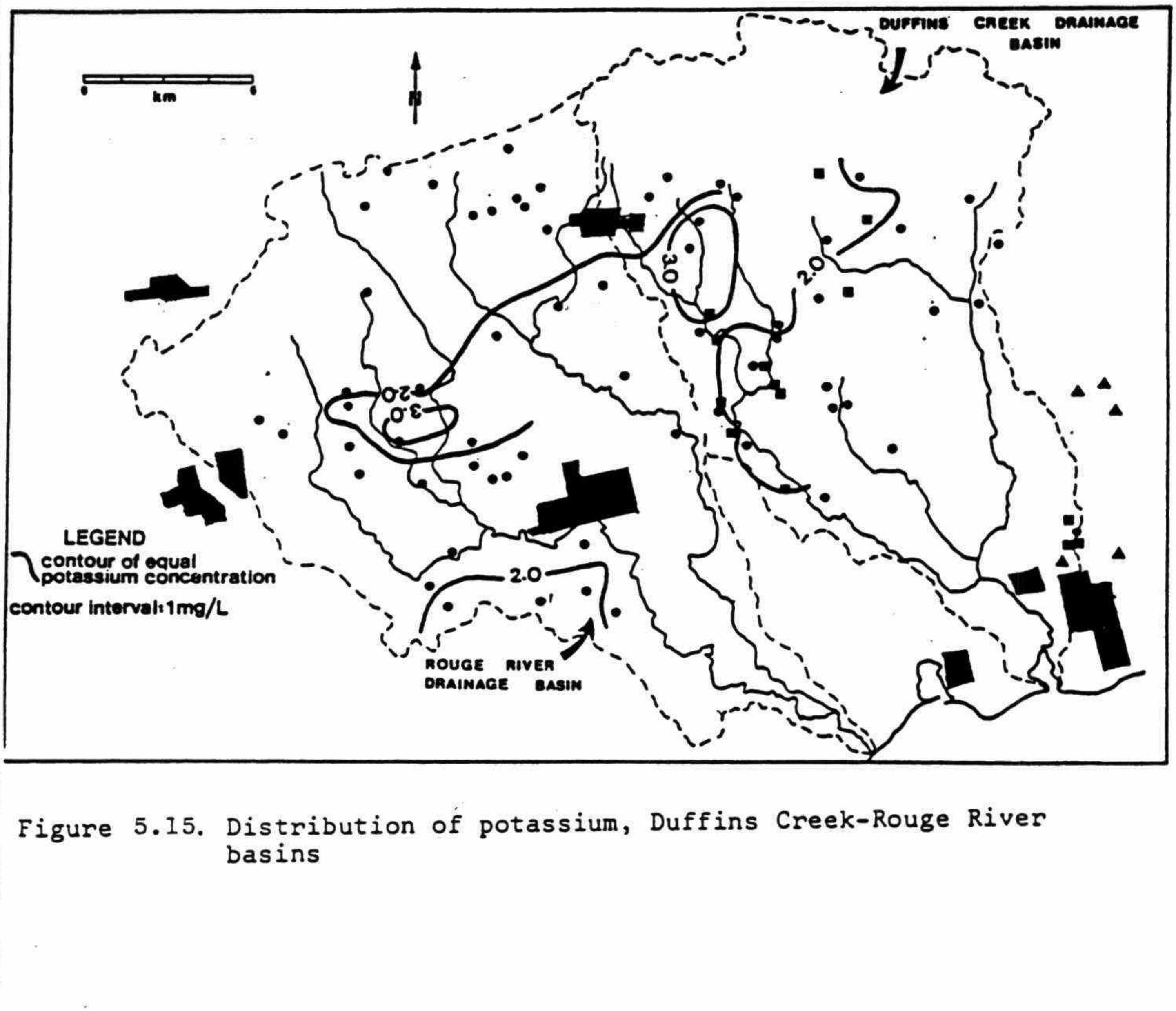
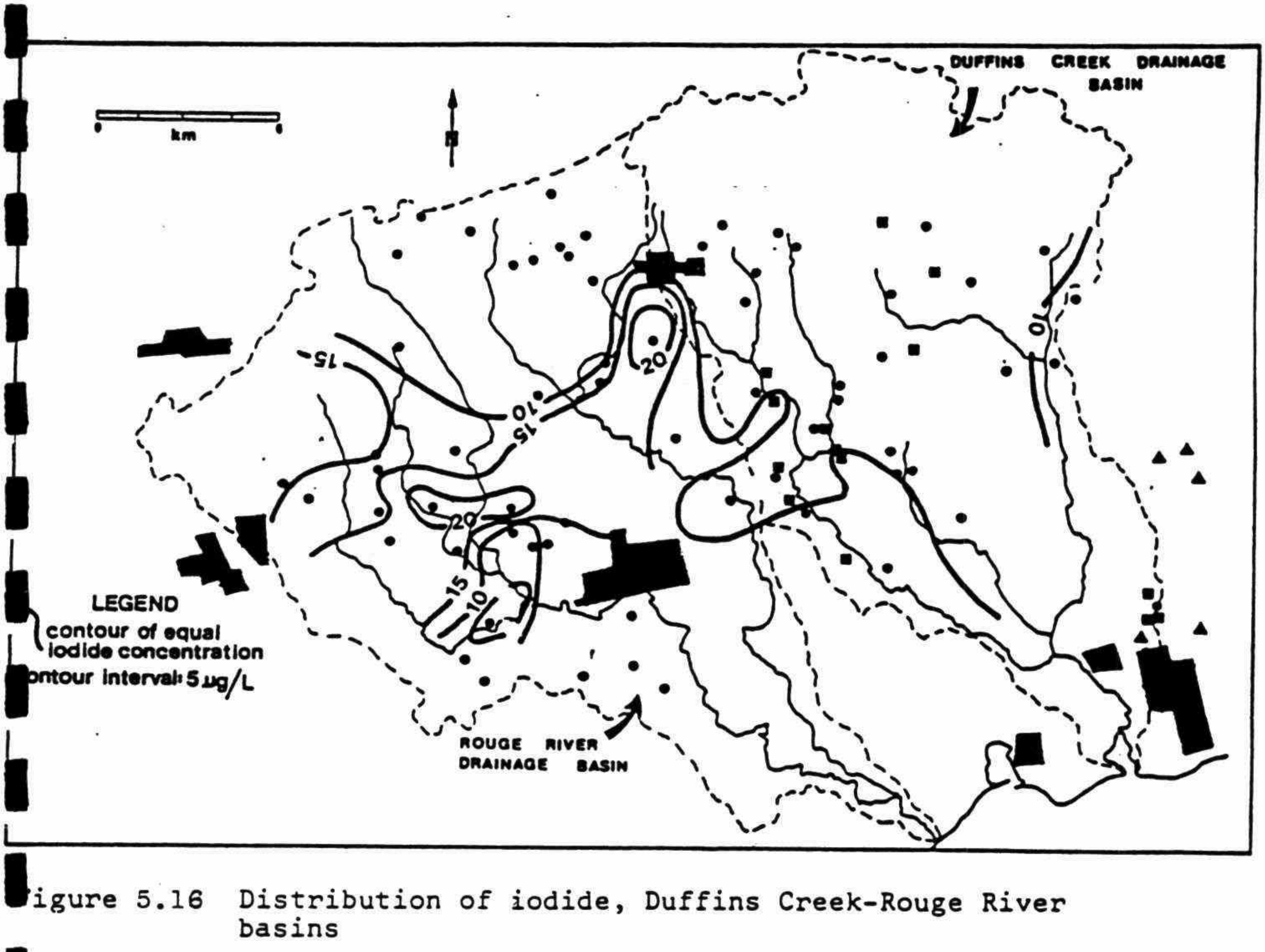

DUFFINS CREEK DRAINAGE BASIN
km
N
3.0
2.0
3.0
2.0
2.0
2.0
LEGEND
contour of equal potassium concentration
contour interval: 1mg/L
ROUGE RIVER DRAINAGE BASIN

Figure 5.15. Distribution of potassium, Duffins Creek-Rouge River basins


DUFFINS CREEK DRAINAGE BASIN
km
N
15
15
10
15
20
20
15
10
5
10
LEGEND
contour of equal iodide concentration
ontour interval: 5 µg/L
ROUGE RIVER DRAINAGE BASIN

igure 5.16 Distribution of iodide, Duffins Creek-Rouge River basins

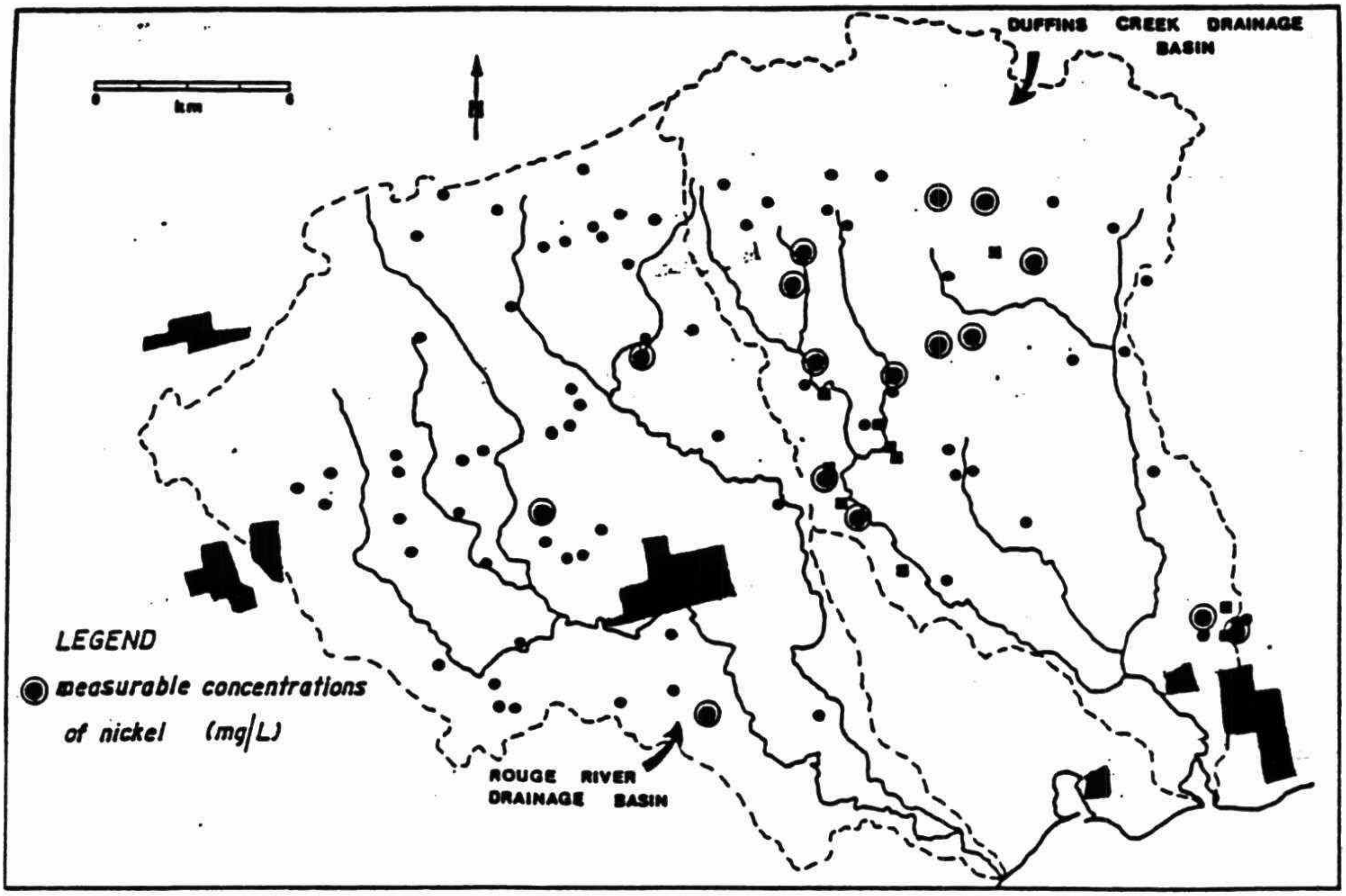

DUFFINS CREEK DRAINAGE BASIN
km
N
LEGEND
◉ measurable concentrations of nickel (mg/L)
ROUGE RIVER DRAINAGE BASIN

Figure 5.17 Distribution of nickel, Duffins Creek-Rouge River basins

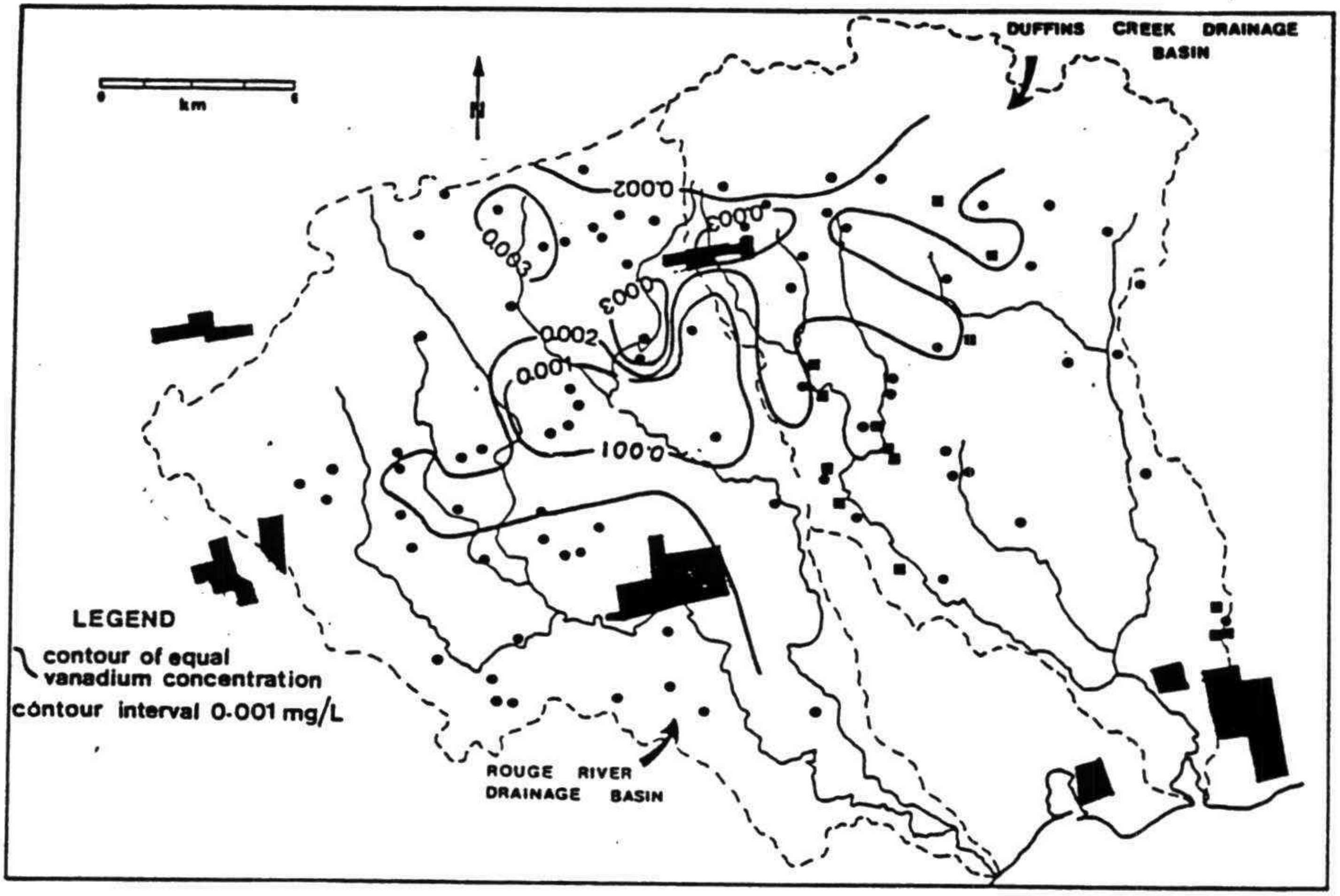

DUFFINS CREEK DRAINAGE BASIN
km
N
0.002
0.003
0.003
0.003
0.002
0.001
0.001
LEGEND
contour of equal vanadium concentration
contour interval 0.001 mg/L
ROUGE RIVER DRAINAGE BASIN

Figure 5.18 Distribution of vanadium

present in measurable concentrations in only a small number of samples and whose distributions appear to be unrelated to the distribution of water types in the basins.

The first group includes manganese, copper, iron, barium, aluminum, vanadium, iodide and potassium. With the exception of vanadium (discussed in Section 5.4.2.10), these chemical parameters exhibit lowest concentrations in Type 1 waters and tend to increase in older Types 2 through 4. This suggests the existence of evolutionary processes of a similar type to that controlling major ion chemistry. In contrast, trace and minor chemical constituents in the second group were detected at only a few sites, the locations of which appear to bear little relationship to the distribution of groundwater types. This group of constituents include nickel, lead, molybdenum, arsenic, selenium, cobalt, cadmium, beryllium, and antimony. Maps of arsenic (Figure VI.1), antimony (Figure VI.2), and nickel (Figure 5.17) are included simply to illustrate the scattered nature of the distributions of this group.

5.2.4.1 Discussion of trace element behaviour

As indicated above, manganese, copper, iron, barium, aluminum, iodide and potassium, show increases in concentration as the waters evolve through Types 1 to 4. The increases in potassium and iodide are thought simply to reflect residence time and the gradual dissolution of available iodide and potassium minerals as the waters move along a flow path. A similar process was proposed by Beck and Howard (1986) for the distribution of fluoride (Figure 5.19).In the case of the trace metals, however, the distributions are more likely to be controlled by redox conditions and the presence of the hydrous oxides of manganese and iron.

The redox conditions of the groundwaters are important because a change in the redox environment can result in i) changes in the oxidation state of the trace metal, ii) changes in the oxidation state of nonmetallic elements such as sulphur and nitrogen with which the trace constituent forms complexes, or iii) changes in the solid mineral phase which can adsorb the trace constituent (Freeze and Cherry, 1979). When trace metals are mobilized under oxidizing conditions, it is usually due to the trace metal forming a soluble complex.

In a reducing environment, trace metals may be mobilized when the hydrous iron and manganese oxides undergo dissolution (Minear and Keith, 1982). These oxides, which occur as partial coatings on silicate minerals in clays, soils, and sediments, act as a "sink" for the heavy metals.

Although it was not possible to obtain reliable redox measurements in the basins, some understanding of the redox character of the water can be inferred from the water chemistry and the hydrogeology of the study area. In recharge areas such as the Oak Ridges moraine, groundwaters tend to be oxidizing, a condition under which certain trace constituents (copper, iron, and manganese, for example) will prefer to remain in the solid mineral phase. In the case of iron, this solid phase could be geothite ($Fe(OH)_3$) or siderite ($FeCO_3$). The presence of elevated manganese, copper, and iron concentrations (Figures 5.11, 5.13, 5.14) at points further along the flow line suggest a slight lowering of redox potential in these older waters, an indication that much of the free

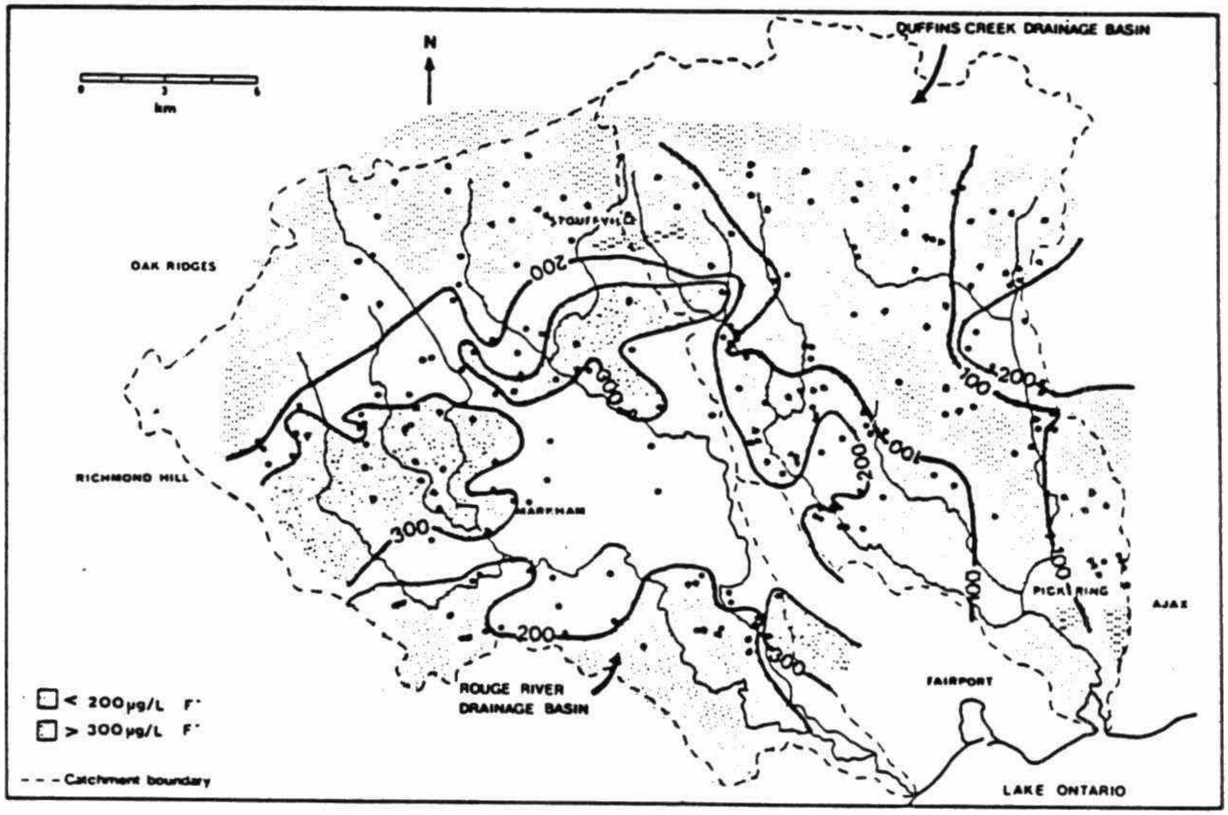


FIGURE 5.19 Fluoride distribution in the Duffins Creek-Rouge River drainage basins (Beck and Howard, 1986)

oxygen has been consumed. Nevertheless, it is clear that these older waters remain at least moderately oxidizing in character, as their is no evidence of either sulphate reduction (in which SO_4 is converted to hydrogen sulphide (HS^-)) or nitrate reduction (in which nitrate is converted to NO_2^- and ultimately to N_2). Drever (1982) has indicated that waters which contain no free oxygen and are not reducing enough to have sulphate reduction occurring, can contain elevated iron and manganese concentrations at levels moderately above 1mg/L.

One element which does not have its concentrations limited under oxidizing conditions is vanadium. This element is stable in groundwaters in both anionic and cationic forms and is most soluble in oxidized groundwater. A map showing the distribution of vanadium in the study area (Figure 5.18) indicates that vanadium concentrations are highest (> 0.002 mg/L) in the recharge areas of the basins and decrease to < 0.0001 mg/L in older waters from the central part of the Rouge River basin.

Not all trace metals will have their concentrations controlled by redox conditions. One of the major controls on barium concentrations is the solubility of barite, $BaSO_4$. At sulphate molar activities of 10^{-3} (SO_4 = 100 mg/L) the corresponding equilibrium molar activity of Ba^{+2} is 10^{-7} (Ba^{+2} = 0.014 mg/L) (Hem, 1970). If the sulphate molar activity decreases to 10^{-5} (SO_4 = 1.0 mg/L) as in the Type 2A through 4A waters, to maintain equilibrium, the barium molar activity must increase to 10^{-5} (Ba^{+2} = 1.4 mg/L). A plot of barium versus sulphate (Figure 5.20) shows how barium concentrations tend to decrease with increasing sulphate concentrations, suggesting that barite solubility may indeed be significant in controlling barium concentrations in groundwaters in the Duffins Creek-Rouge River basins.

Distributions of certain trace metals including arsenic, antimony, nickel, lead, beryllium, molybdenum, chromium, and cadmium appeared to be random, with locally elevated concentrations bearing no relation to the distribution of the groundwater types in the basins. For example, arsenic, antimony, and nickel concentrations were below the ICP (pre-concentrated) determination limits for these elements in almost all the groundwater samples; the only samples having significant (essentially ICP-measurable) arsenic, antimony, and nickel concentrations were those classified on the basis of their major and minor ion chemistry as contaminated Type 1 (1S, 1U, and 1N) waters. Type 1S waters contained elevated nickel concentrations while Type 1U and 1N waters contained considerably elevated arsenic and antimony concentrations relative to all other water types.

For arsenic, antimony and nickel, there are several factors which limit the solubility of these elements in groundwater. Low arsenic concentrations in most groundwaters are probably due to the low solubility of $HAsO_4^{-2}$, which is the commonest arsenate species at pH values greater than 7.2. In addition to this, arsenic solubility in groundwaters is limited by the sorption of arsenate AsO_4^{-3} on hydrous iron oxides. Nickel in the 2+ oxidation state (Ni^{+2}) is soluble and is highly mobile. It also forms soluble complexes with sulphate, and chloride. However, in oxidizing environments, nickel may undergo fixation (adsorption) by iron and manganese oxides while in reducing conditions nickel is precipitated as nickel sulphide.

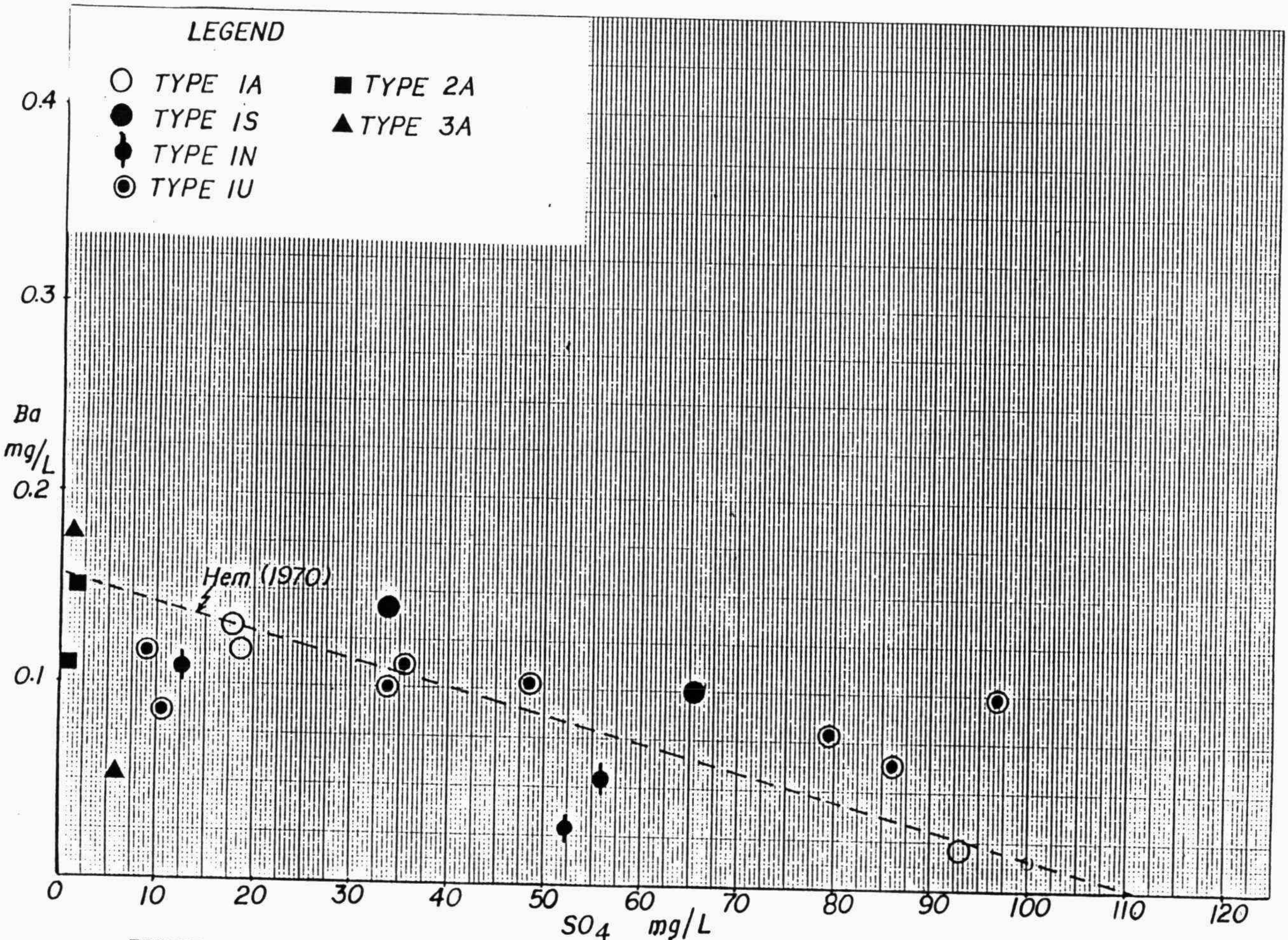


FIGURE 5.20 Plot of barium vs sulphate, Duffins Creek-Rouge River basins groundwaters

The solubility controls for antimony are not as well understood as those of arsenic and nickel. In oxidizing conditions antimony in the form Sb^{+5} is stable. Minear and Keith (1982) suggest that the most important factor influencing antimony concentrations in water may be adsorption on clays and hydrous oxides.

Of the remaining trace elements that were found to display sporadic distributions, (chromium, lead, molybdenum, cadmium, cobalt, selenium, and beryllium) only chromium, beryllium and molybdenum were ever present in measurable concentrations. Cadmium, lead, cobalt and selenium were all below ICP determination limits. Factors influencing the solubilities of these metals are discussed below.

In most cases, only the contaminated waters (Types 1S, 1N, and 1U) showed the presence of chromium, usually at concentrations fractionally above the ICP determination limit. With a few exceptions in the older waters, chromium was not detected. From a geochemical standpoint, the most significant control on the concentration of chromium in groundwaters is the redox characteristic of the groundwater system. In oxidizing groundwaters such as Type 1 waters, Cr^{+3} will be oxidized to Cr^{+6} in the form $HCrO_4^-$ (chromate) which is stable in the pH range of 6.5 to 8.5. However, this reaction proceeds very slowly and it is possible that much of the chromium in groundwaters undergoes other reactions such as adsorption prior to oxidation. One interesting feature is the occasional association of low chromium concentrations with elevated iron concentrations in the older Type 2A through 4A groundwaters. Minear and Keith (1982) indicate that ferrous iron will reduce Cr^{+6}, lowering the concentration of chromium. This reduction is dependent upon several factors including the ferrous iron concentration, the pH, and the degree of oxidation of the ferrous iron by the oxygen in the water.

Only two of the 107 groundwater samples contained measurable lead concentrations. While this is partly explained by the poor level of detection for lead using ICP-AES, it is also due to the low solubility of lead in oxidizing groundwaters containing bicarbonate and sulphate. Under such conditions, lead will form the complexes $PbCO_3$ and $PbSO_4$, both of which have low solubilities in a high redox environment. In reducing environments, lead will form the sulphide compound PbS. Hem (1970) states that under such conditions it is likely that these solubility constraints could limit the concentration of lead to about 0.002 mg/L (2ug/L), well below the ICP determination limit of 0.23 mg/L (0.023mg/L for the pre-concentrated samples).

Beryllium concentrations in many groundwater samples from the study area are below 0.0001 mg/L (0.1 ug/L). In the remaining samples, Type 1A recharge waters showed slightly higher beryllium concentrations (< 0.0008 mg/L) than the older Type 2 through 4A groundwaters (0.003 - < 0.0001 mg/L). However, groundwaters with the highest beryllium concentrations (0.0031 - < 0.0001) are those classified as contaminated (1U, 1S, and 3U) waters. The concentrations of beryllium in all Duffins Creek-Rouge River basins water samples are within the range expected for uncomplexed Be^{+2} at a pH of 7. Many beryllium oxide and hydroxide species have considerably lower solubilities.

Only two groundwater samples contained measurable concentrations of molybdenum while none of the groundwater samples contained measurable concentrations of cobalt, cadmium and selenium. Unfortunately, molybdenum is a rare element and little is known about geochemical controls on its solubility.

Cobalt concentrations in groundwater may be limited by several factors. In the presence of bicarbonate and at a pH of 8, $CoCO_3$ will limit cobalt solubility to 0.006 mg/L, well below the ICP determination limit of 0.017 mg/L. The most significant control on cobalt solubility is adsorption by colloidal particles of hydrous oxides of manganese and/or iron present in aquifer materials (Jenne, 1968).

Cadmium concentrations in oxidizing groundwaters are likely restricted as a result of the formation of $CdCO_3$ and $Cd(OH)_2$, both of which have very low solubilities, while the formation of CdS is the controlling solid phase in reducing environments (Minear and Keith, 1982).

The small amount of information available on solubility controls of selenium concentrations suggests that redox conditions may be the most important limiting factor. Under oxidizing conditions selenium is present in groundwaters in the form SeO_3^{-2}.

5.2.5 Summary of trace metal behaviour

A chart summarising typical concentrations of the 19 trace constituents in the 4 water types is shown in Table 5.1. It should be emphasised that this is a summary diagram and is designed to provide, in a much generalised form, the level or range of levels at which the trace metal may be expected to occur in a particular water type. When single values are given without a range, it is usually because only one valid measurement was made for that particular water type.

Based on trace element distribution maps and Table 5.1, the following summary observations can be made:

1) The distributions for several trace metals (barium, copper, boron, aluminum, manganese, iron, and vanadium, for example) are similar to the groundwater type distribution, suggesting that these parameters are most strongly influenced by natural chemical processes;

2) Type 1 (1A, 1S, 1N, 1U) recharge groundwaters are naturally characterized by elevated concentrations of vanadium (> 0.002 mg/L) and chromium (0.0023 mg/L);

3) Groundwaters classified on the basis of major and minor ion chemistry as older ion exchange Type 2 through 4 waters contain elevated concentrations of manganese (>0.02 mg/L), iron (>0.3 mg/L), copper (> 0.02 mg/L), boron (>0.02 mg/L), aluminum (> 0.03 mg/L), and barium (> 0.1 mg/L). The elevated concentrations of most of these trace elements is likely due to slight changes in redox potential of the older, naturally evolving groundwaters.

4) The distributions of some trace elements (e.g. arsenic, selenium, nickel, and antimony) are not related to groundwater type, suggesting that other processes such as contamination control their concentration in these waters;

Table 5.1 Summary of typical trace element concentrations in the groundwaters types of the Duffins Creek-Rouge River basins

	TYPE 1				TYPE 2		TYPE 3		TYPE 4	
Element	1A	1S	1N	1U	2A	2U	3A	3U	4A	4U
Manganese	<0.02	>0.03	<0.014	<0.03	>0.02		>0.02		>0.02	
Phosphorous	<0.017	<0.017	<0.017	0.07	0.0288		0.1676		0.12	
Molybdenum	<0.0034	<0.0034	<0.0034	<0.0034	<0.0034		<0.0034		<0.0034	
Aluminum	<0.008	0.034	<0.03	<0.03	>0.01		>0.03		<0.03	
Zinc	>0.01	>0.007	>0.02	>0.003	>0.007		>0.003		>0.02	
Nickel	<0.0068	0.124	0.009	0.011	<0.0068		<0.0068		<0.0068	
Iron	<0.3	<0.3	<0.3	0.455	>0.3		>0.3		>0.3	
Lead	<0.023	<0.023	<0.023	<0.023	<0.023		0.023		<0.023	
Cobalt	<0.017	<0.017	<0.017	<0.017	<0.017		<0.017		<0.017	
Cadmium	<0.016	<0.016	<0.016	<0.016	<0.016		<0.016		<0.016	
Arsenic	<0.0113	>0.0113	>0.0113	>0.014	<0.0113		0.0113		<0.0113	
Selenium	<0.0211	<0.0211	<0.0211	<0.0211	<0.0211		<0.0211		<0.0211	
Antimony	<0.0188	<0.0188	<0.028	<0.028	<0.0188		<0.0188		<0.0188	
Vanadium	>0.002	>0.003	>0.002	>0.002	<0.001		0.001		<0.001	
Beryllium	<0.0008	<0.0009	<0.0001	<0.0014	<0.0008		<0.0001		<0.0003	
Barium	<0.1	>0.1	<0.1	<0.1	>0.1		>0.1		<0.1	
Chromium	<0.0023	0.0023	0.0029	0.0023	<0.0012		>0.0012		<0.0012	
Boron	<0.0023	>0.02	>0.02	>0.02	>0.02		>0.04		<0.0023	
Copper	<0.03	<0.03	<0.03	<0.03	>0.03		>0.03		>0.03	

< less than; > greater than

5) Type 1 contaminated groundwaters (1S, 1U, and 1N) are characterized by elevated concentrations of nickel (0.01 mg/L), arsenic (> 0.0113 mg/L), antimony (0.02 mg/L);

6) Concentrations of cobalt, cadmium, and selenium are below ICP determination limits for these elements in all groundwaters analyzed.

5.3 Analysis of potential contaminant sources

5.3.1 Introduction

For this part of the study, it was appropriate to focus on two types of non-point source contamination: man-made "surface" sources which undergo chemical modification during entry into the groundwater flow system, and natural sub-surface sources which cause contamination by direct mixing. Three types of man-made contaminant were investigated: road de-icing chemicals, inorganic and organic fertilizers, and landfill leachates. In the natural source category, various types of saline bedrock water were investigated. In all, a total of 42 contaminant samples were submitted for major, and minor ion analyses. 17 of these were also submitted for trace constituent analysis by ICP-AES. As indicated in Section 4.2.2.6, road de-icing chemicals were submitted as 5% solutions, while the inorganic fertilizers were analyzed in 10% solutions. Results of the chemical analyses are presented in Appendix III.

Samples submitted for trace constituent analysis included 1 landfill leachate, 9 bedrock waters, 4 inorganic fertilizers and 3 road de-icing chemicals. The major, minor and trace constituent chemistry of each contaminant is discussed below in Sections 5.3.2, 5.3.3. and 5.3.4. respectively.

5.3.2 Major ion chemistry

The major ion chemistry of representative samples of the four principal types of potential contaminant is displayed on modified Schoeller plots in Figures 5.21a and 5.21b. Major differences are indicated. For example, the road salts are shown to be extremely pure consisting of sodium (or in the case of $CaCl_2$, calcium) and chloride with only minor amounts of sulphate, potassium, magnesium, nitrate and bicarbonate. This is in contrast to the other surface sources of contamination investigated, all of which exhibit considerable variation in their major ion chemistry.

Two types of bedrock water are represented on Figure 5.21b. Low chloride waters from the Duffins Creek-Rouge River drainage basins (generally $< 10^2$ mg/L Cl) and high chloride waters from deep formations in west-central and southwestern Ontario ($10^3 - 10^5$ mg/L Cl). As indicated in the figure, the waters exhibit distinctly different major ion chemical characteristics. The high chloride waters are relatively pure and are dominated by NaCl; the low chloride waters tend to retain a calcium bicarbonate character.

There are clearly many ways in which the four principal contaminants can be distinguished chemically at source. Several examples of plotting procedures are shown in Figures 5.22 to 5.24. Figures 5.22 and 5.23 display plots of the ratios Na/Ca vs Ca and Cl/NO_3 vs NO_3 respectively for the four principal types of contaminants studied. In most cases, these contaminants occupy distinctive areas of the diagram. Nevertheless, some interesting features may be noted. For example, while as expected, the high chloride bedrock are clearly distinguishable from the low chloride waters by virtue of their high Na/Ca ratios, it is significant that the phosphate fertilizers also exhibit similarly high Na/Ca ratios (10^{+2}). Also, while both inorganic and organic fertilizers (sewage sludges) are distinguished from other potential contaminants investigated by their low Cl/NO_3 (10^{-1}) ratios (Figure 5.23), the level of enrichment of nitrate relative to chloride in the organic fertilizers is one to four orders of magnitude lower than that of the inorganic fertilizers. The greatest nitrate enrichment is generally shown by the hog and dairy cow manures. All other potential contaminants investigated have high relatively Cl/NO_3 ratios (10^{+1} to 10^{+3}). The inorganic fertilizers are also characterized by elevated

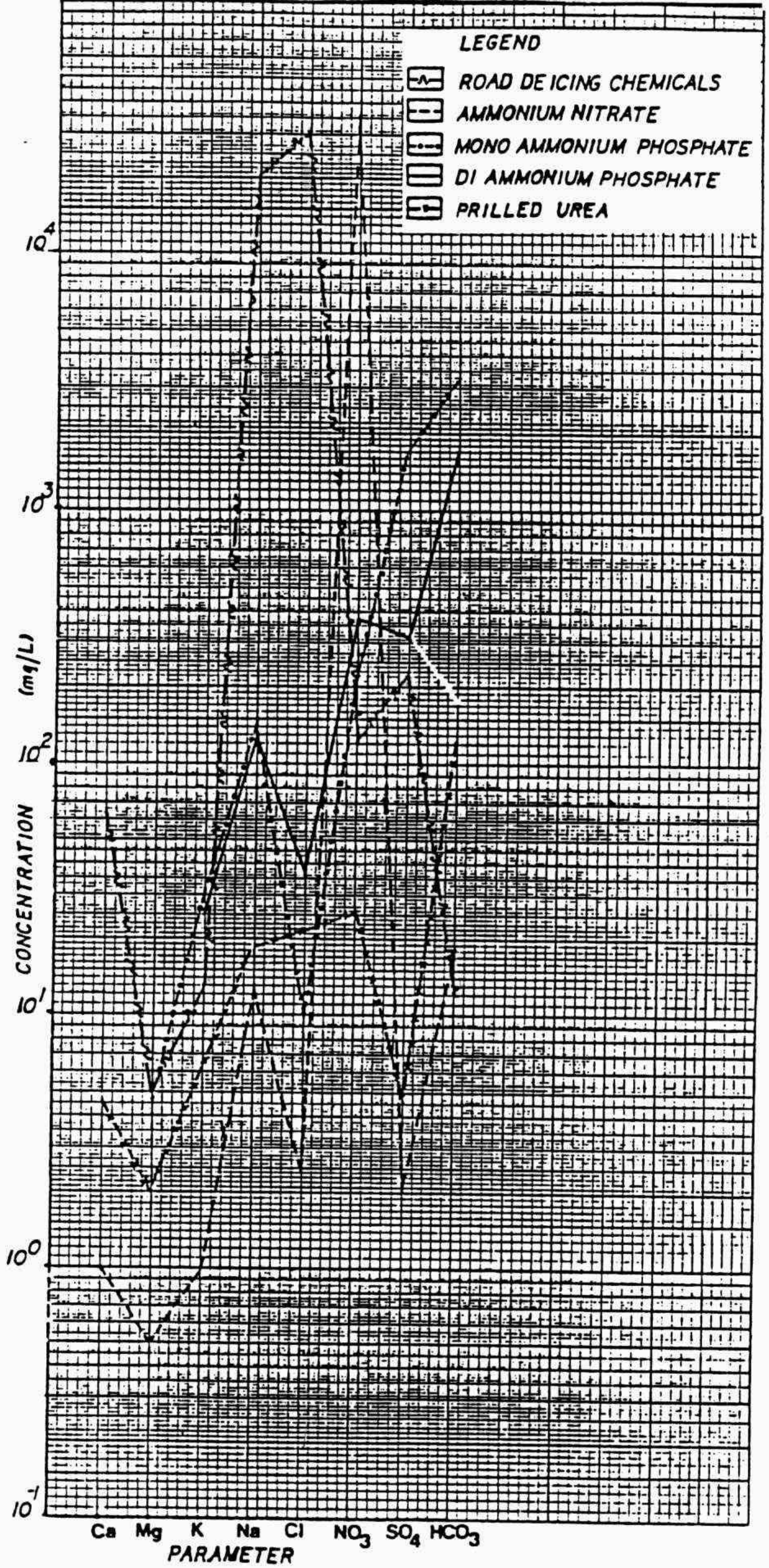


Figure 5.21a Schoeller plot of major and minor ions, potential contaminants

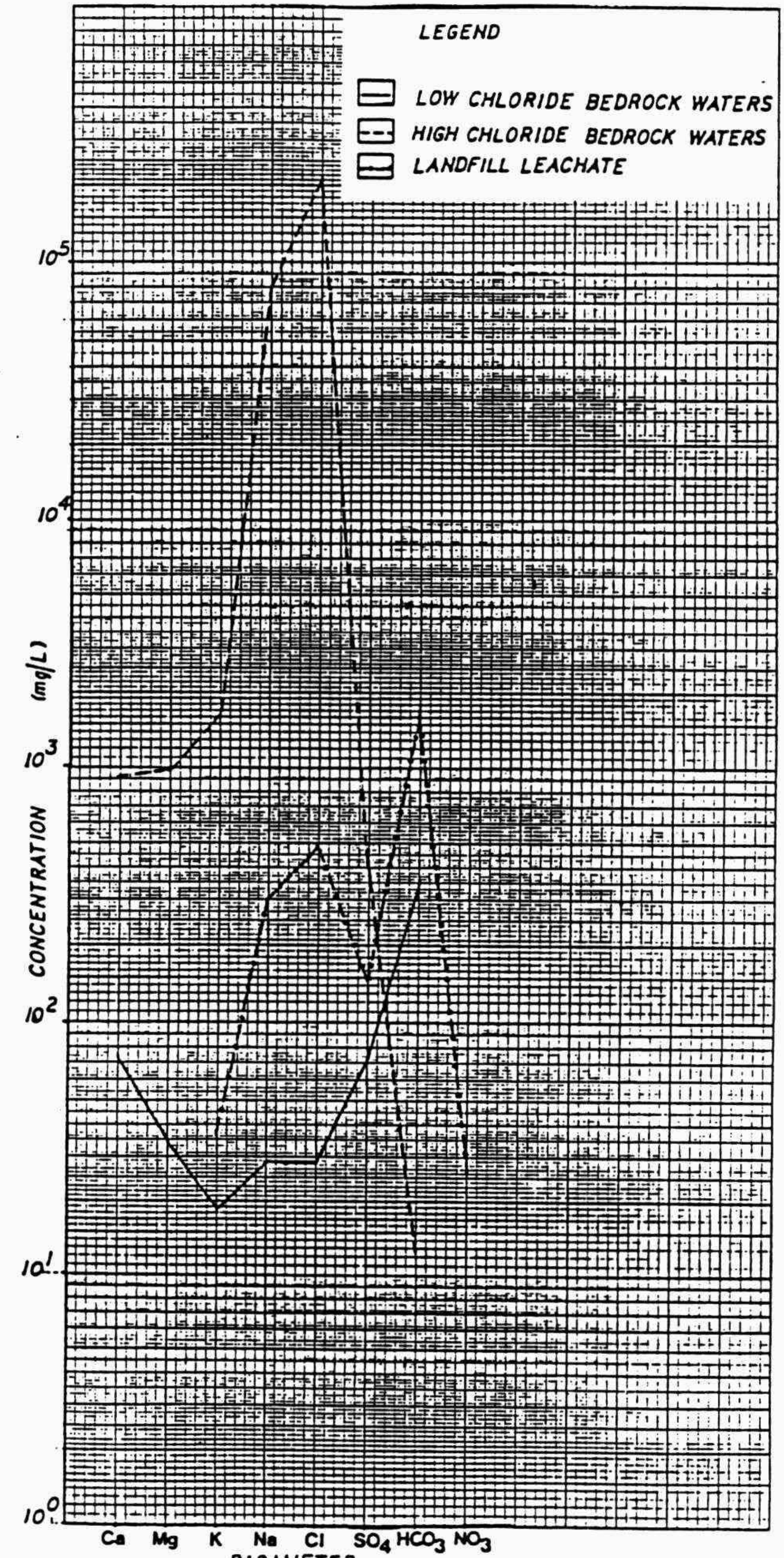


FIGURE 5.21b Schoeller plot of major and minor ions, potential contaminants

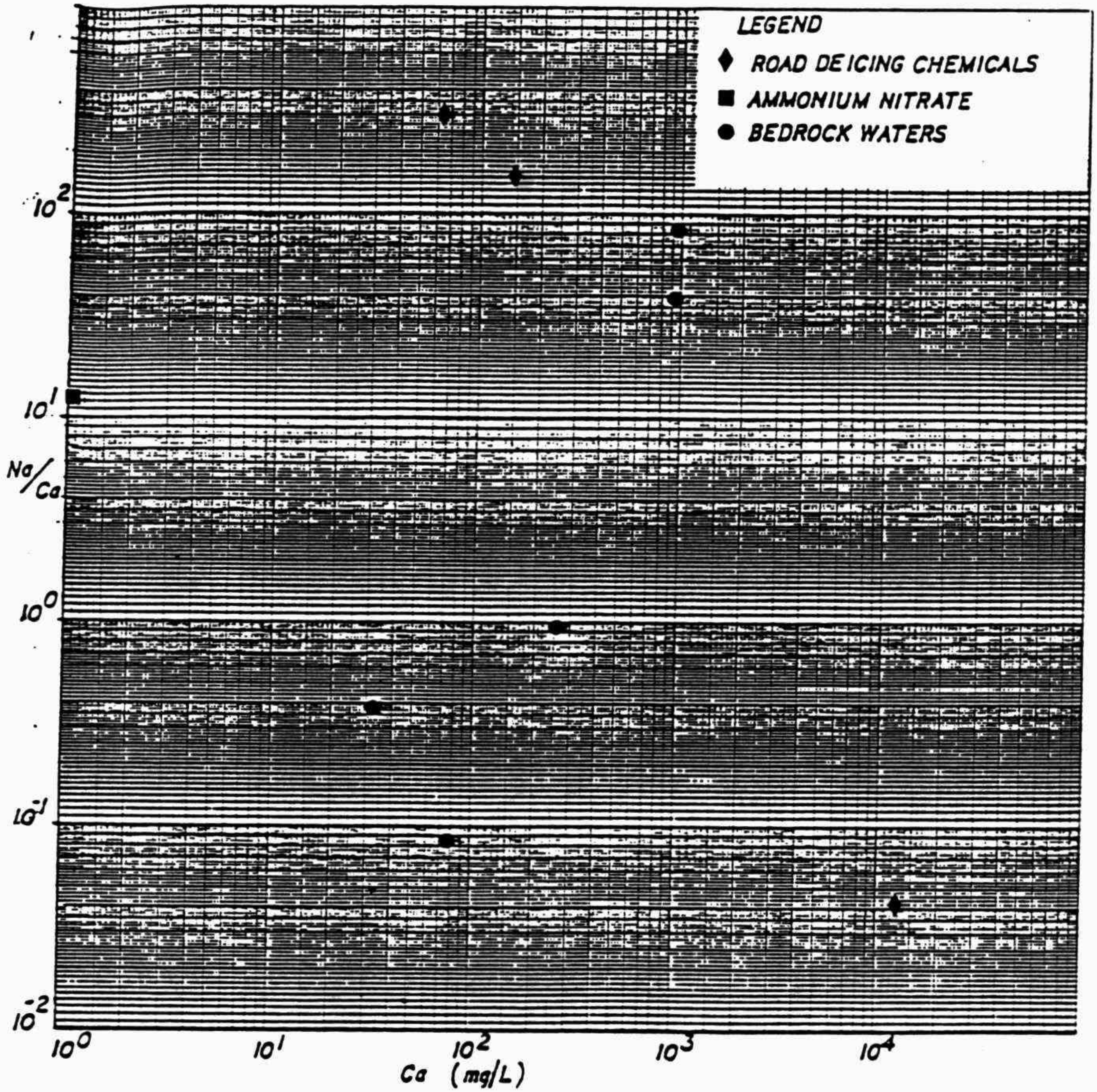


Figure 5.22 Plot of Na/Ca vs Ca for potential contaminants

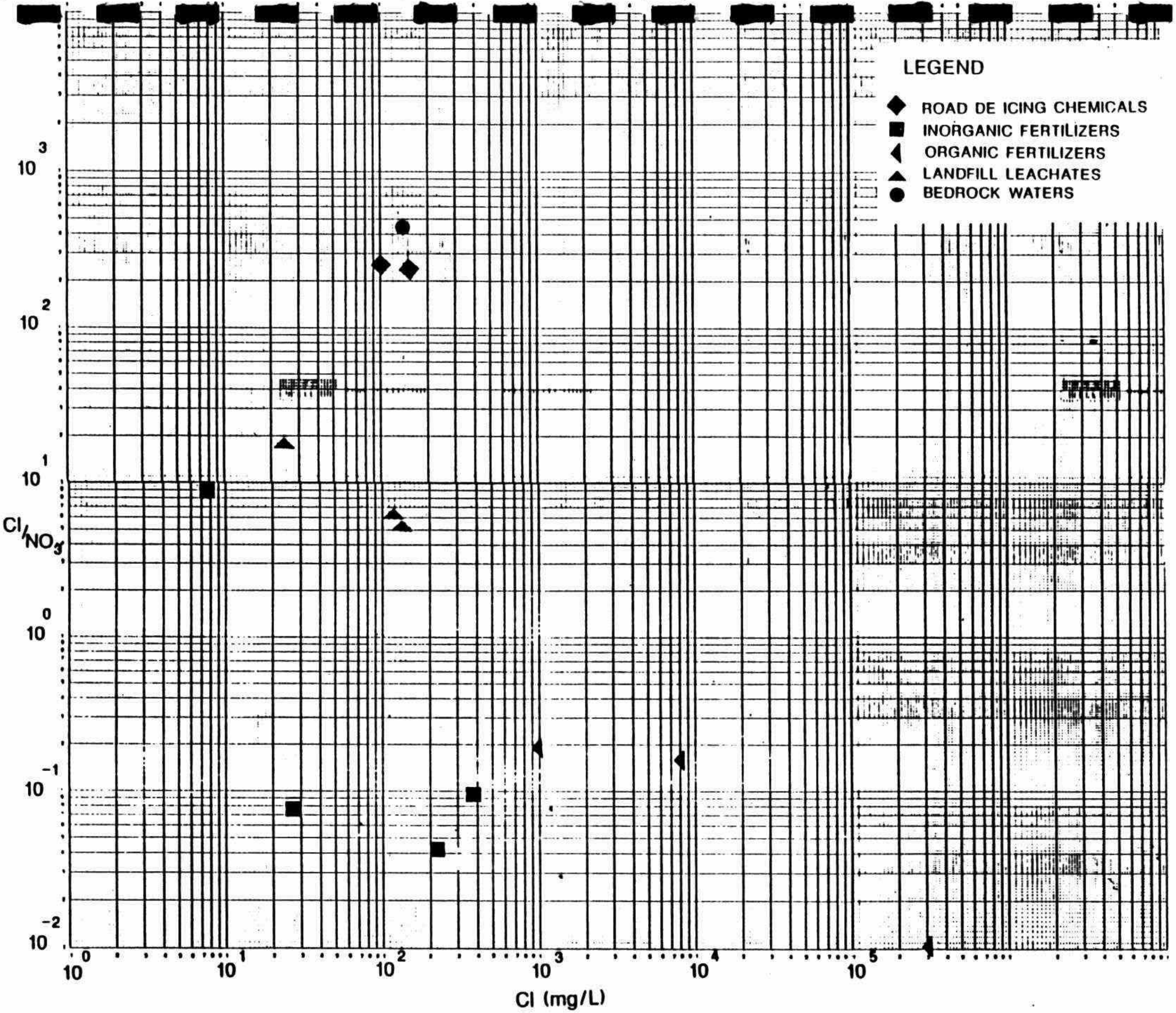


Figure 5.23 Plot of Cl/NO_3 vs NO_3 for potential contaminants

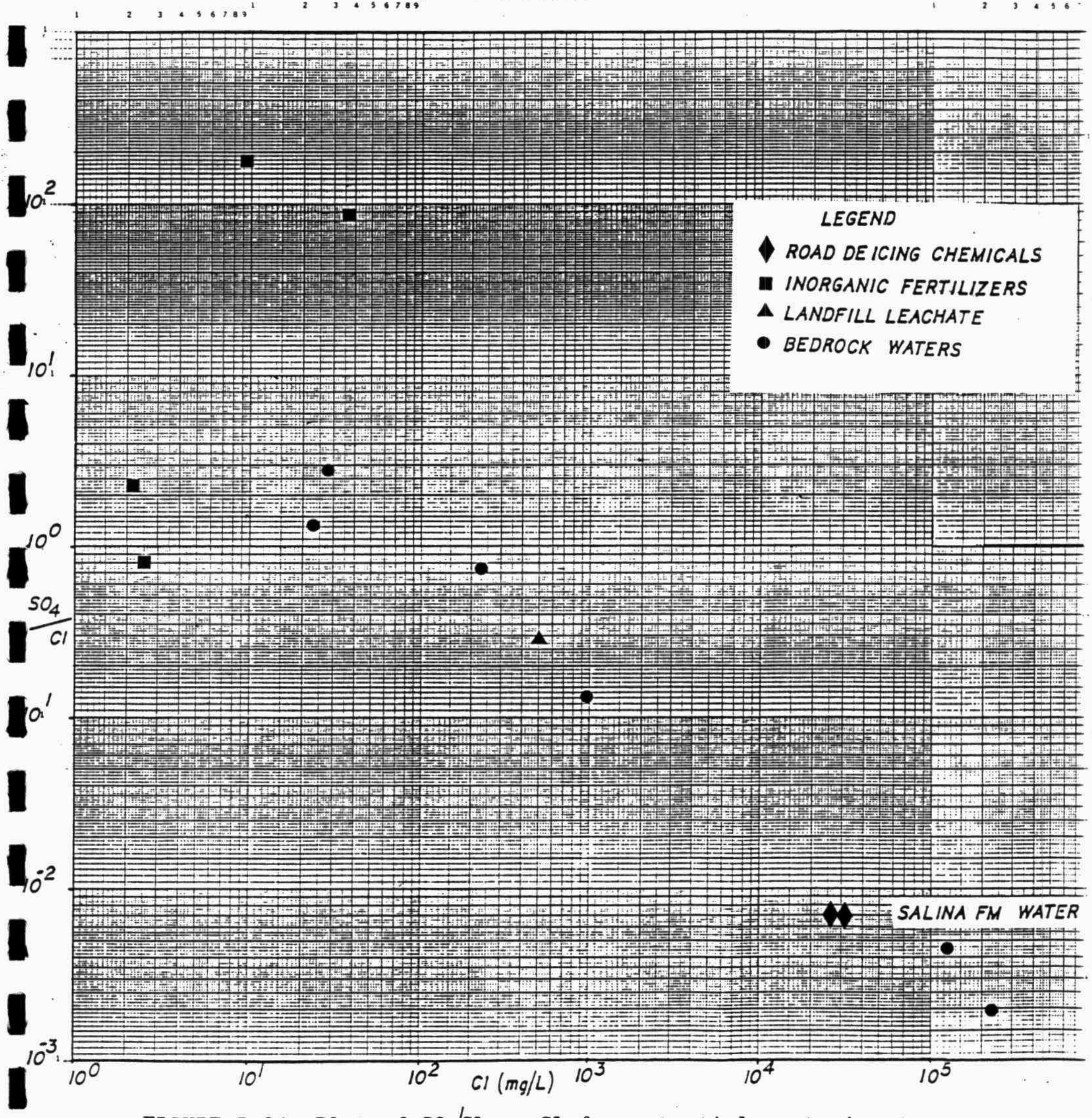


FIGURE 5.24 Plot of SO_4/Cl vs Cl for potential contaminants

sulphate concentrations as indicated by their SO_4/Cl ratios. These ratios are plotted in Figure 5.24. The road salts, landfill leachates and bedrock waters are generally characterized by a depletion in sulphate relative to chloride.

All potential contaminants with the exception of the road salts exhibit enrichment in bicarbonate relative to nitrate. Landfill leachates, in particular, show enrichment in bicarbonate. In the Clark and Piskin (1976) study of 123 landfill leachates, high alkalinity was noted as a characteristic of many leachates. Ⓥ It is believed that the high alkalinity (hydroxide, carbonate and bicarbonate ions) occurs during decomposition of organic wastes in landfills. Decomposition releases large amounts of CO_2 to both the leachate and to the atmosphere through the fill covering the landfill. The carbon dioxide forms carbonic acid (H_2CO_3) which contributes to alkalinity by forming HCO_3^-.

5.3.3. Minor anion chemistry

Evaluation of the minor anion chemistry focused chiefly on the presence of iodide and its relationship to chloride. Figure 5.25a shows plots of iodide versus chloride for the four principal types of contaminant. Representative samples are also plotted on Figure 5.25b which shows a plot of I/Cl versus the chloride concentration. For the purpose of comparison, Figure 5.25b also includes two dilution lines. Line A represents the chemical mixing of an uncontaminated Type 1A recharge water with a 5% solution of road salt (NaCl), and line B represents a similar mix with a saline bedrock water.

Ⓡ The diagrams indicate that road de-icing chemicals (NaCl and $CaCl_2$) are significantly depleted in iodide with respect to seawater. All other contaminants compared in the same way, exhibit a relative enrichment in iodide. As uncontaminated groundwaters undergo increased mixing with the 5% road salt solution (Figure 5.25b), the iodide ratio reduces rapidly, achieving the ratio in sea water at a chloride concentration of only 600 mg/L. Uncontaminated groundwaters which undergo chemical mixing with saline bedrock water (dilution line B) remain considerably enriched in iodide relative to seawater.

It is interesting to note that while the majority of the bedrock waters are strongly enriched in iodide, two samples on Figure 5.25b show a strong depletion. One sample was collected from the Salina Formation which is an important source of road salt in southern Ontario; thus the iodide depletion may be explained by the presence of iodide depleted rock salt in the formation. The second sample was obtained from the Rochester Formation and is most likely to have been depleted in iodide by ion exchange or precipitation processes (Beck and Howard, 1986).

5.3.4. Trace element chemistry

Trace element data for the four principal contaminant sources are presented in the form of modified Schoeller diagrams in Figures 5.26 and 5.27. Selected data are also contained in Tables 5.2, 5.3 and 5.4.

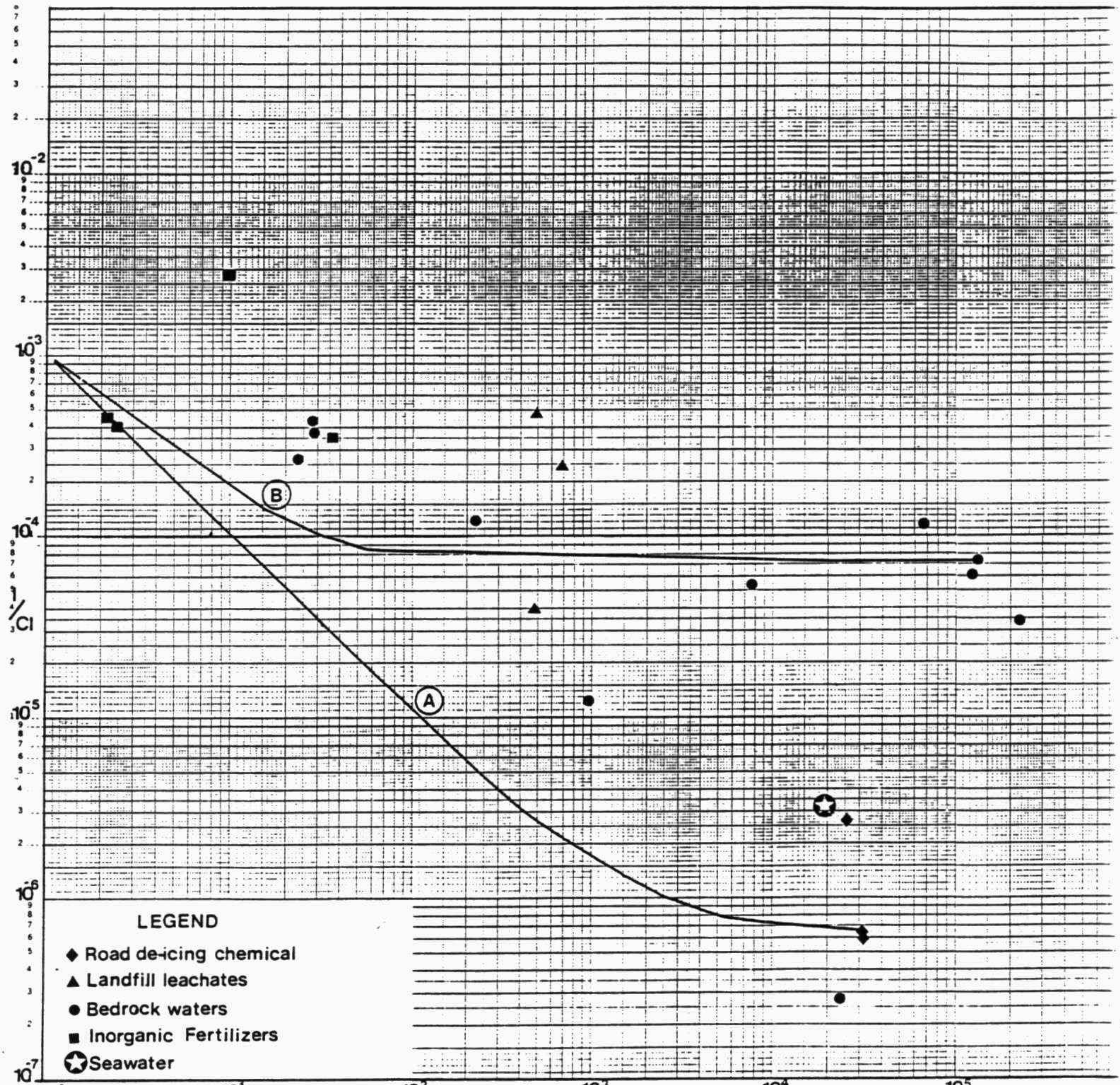


FIGURE 5.25b Plot of I/Cl vs. Cl for the potential contaminants

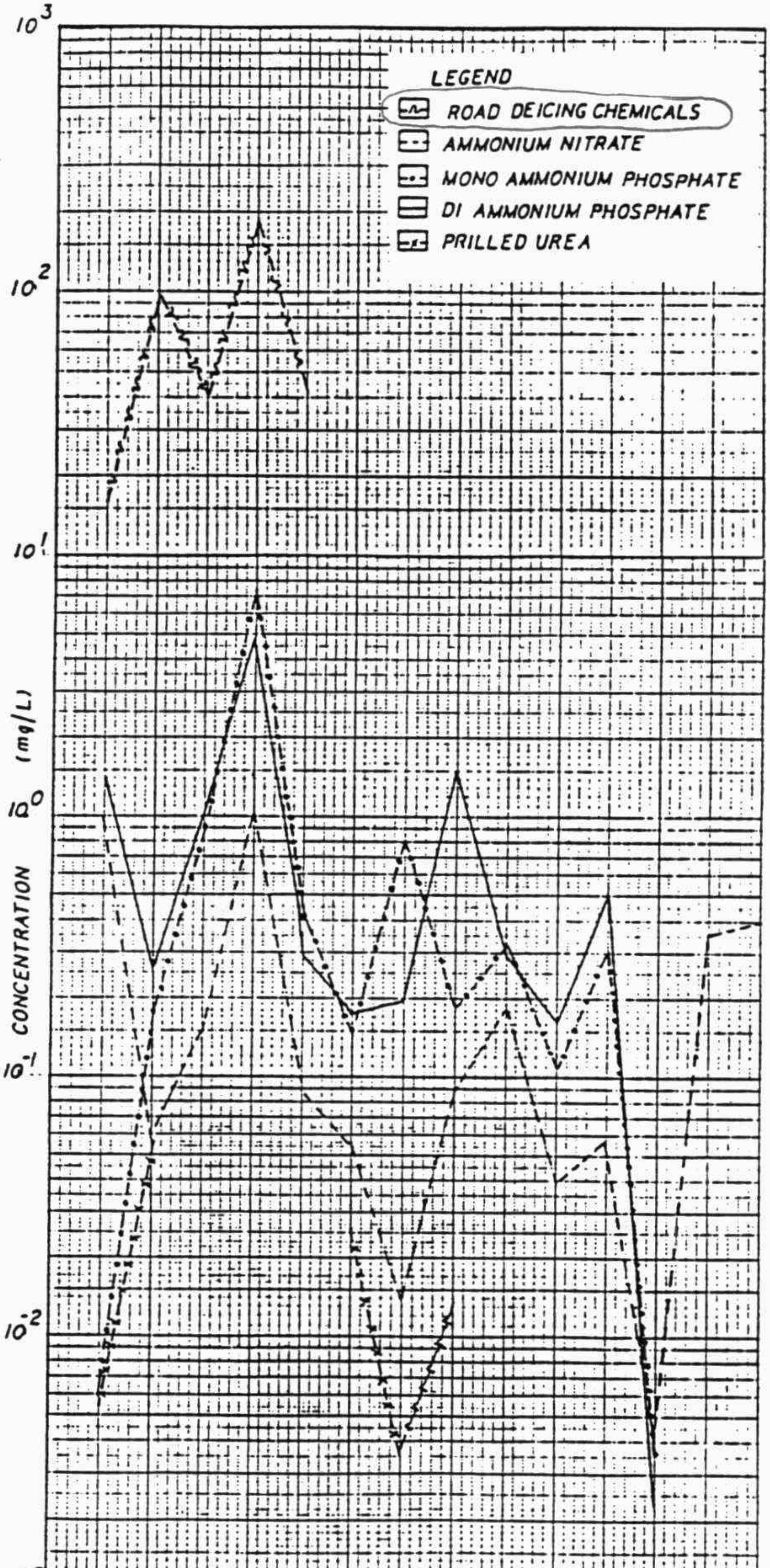


FIGURE 5.26 Schoeller plot of trace elements, potential contaminants

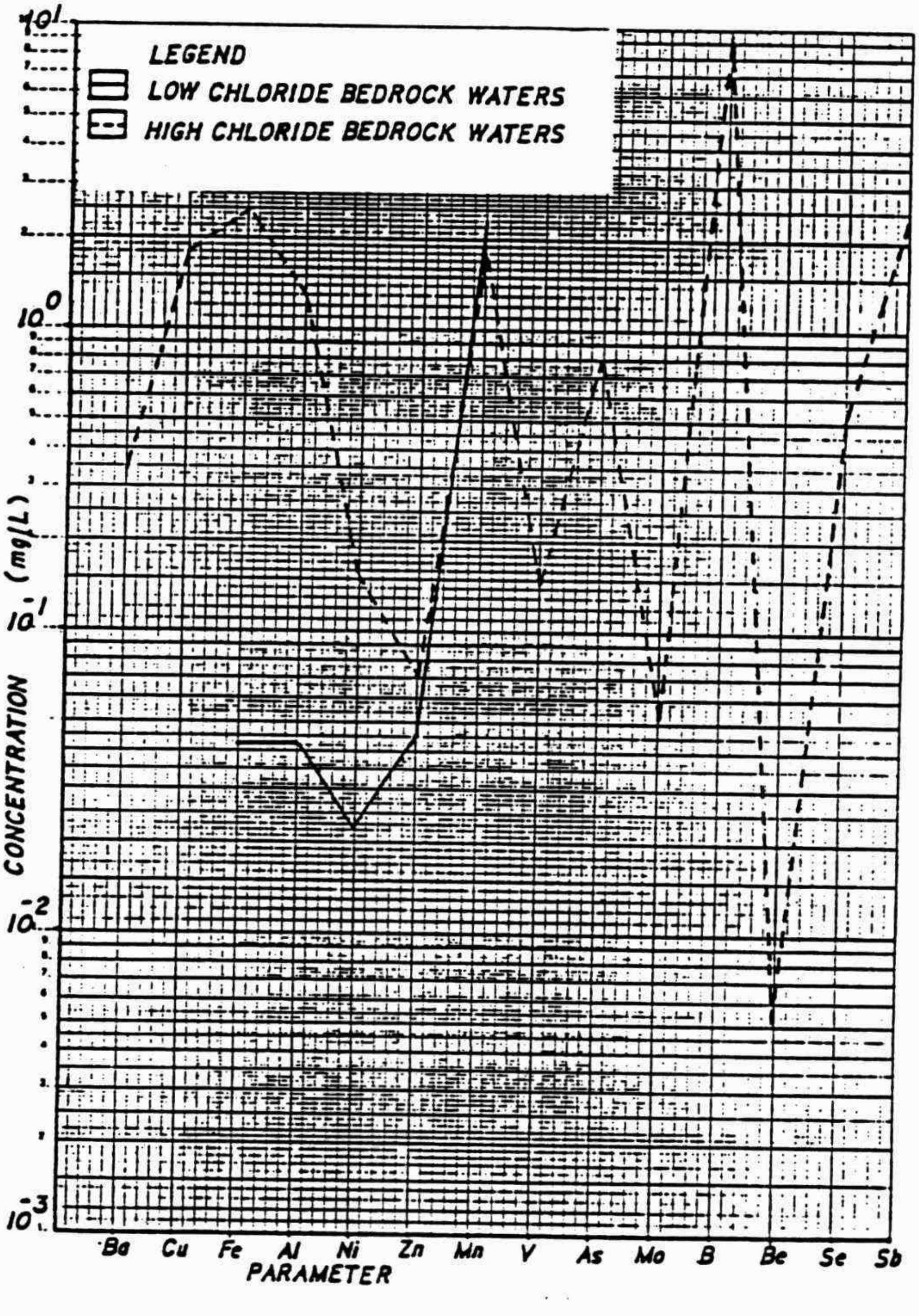


Figure 5.27 Schoeller plot of trace elements potential contaminants

As demonstrated in Section 5.3.3, the major ion analyses of the road de-icing chemicals ($NaCl$ and $CaCl_2$) indicated an unusually high degree of chemical purity. This conclusion is further supported by the trace element analyses which showed measurable concentrations of only 5 of the 20 analysed trace elements. As shown in Figure 5.26, the trace impurities identified were common to both $NaCl$ and $CaCl_2$, and included barium, aluminum, nickel, iron, and copper. The concentrations of these trace constituents in 5% solutions of the road de-icing chemicals are given in Table 5.2. In general, $CaCl_2$ contains a higher copper concentration than $NaCl$, but lower concentrations of barium and aluminum.

Table 5.2 Trace constituents in Road De-Icing Chemicals

Element	$NaCl$ 5% Solution (mg/L)	$CaCl_2$ 5% Solution (mg/L)
Al	166.7-181.0	92.1
Ni	42.3- 58.9	57.9
Fe	42.2- 58.8	57.8
Cu	98.2-154.5	251.9
Ba	7.4- 15.9	4.8

In contrast to the road salts, the other three potential contaminants exhibit a wide range of trace element impurities (Figures 5.26 and 5.27). The phosphate and nitrate fertilizers were found to contain different suites of trace elements which presumably reflects the different source materials used in the manufacture of fertilizers. The nitrate fertilizers are generally distinguished from the phosphate fertilizers by measurable concentrations of lead, cobalt, chromium, selenium, and antimony. However, several other trace element characteristics of the inorganic fertilizers to note include:

1) The phosphate fertilizers are characterized by manganese enrichment relative to zinc, in contrast to nitrate fertilizers, road salts, low chloride bedrock waters and landfill leachates all of which have Mn/Zn ratios of less than 1.

2) Di-ammonium phosphate, and ammonium nitrate fertilizers can be distinguished from the prilled urea and mono-ammonium phosphate fertilizers, road salts and bedrock waters by their elevated concentrations of barium relative to copper, nickel, and iron.

The sewage sludge samples were not submitted for trace element analyses due to difficulty in filtering the samples during sample preparation. Consequently, literature values were used to supplement laboratory analyses; these are shown in Table 5.3.

The bedrock waters also exhibited considerable variability in their trace element chemistry as shown in Figure 5.26b. When dilution is taken into account and the data are normalised according to the chloride concentrations, bedrock waters are distinguished from road salts by the presence of measurable concentrations of manganese, phosphorous, molybdenum, zinc, lead, cobalt, chromium, cadmium, arsenic, selenium, antimony, vanadium, boron, and beryllium.

Table 5.3 Minor and trace constituents in various manure sludges

			Parameter (mg/L)				
Manure Type	Fe	B	Mn	Cu	Zn	P	K
Poultry		60	350	25	250	9000	7000
Beef			100				
Hog	300			200	750	2500	4000
Dairy		15				500	6000

* (from Webber, 1982)

Table 5.4 Trace Constituents in Landfill Leachate

Element	Range of Concentration	Typical Landfill Leachate Composition	Mountain Rd Landfill Leachate Composition
As	0 -5500	0.038	0.1140
Al	0 - 122	0.27	<0.0082
Ba	0 - 5.4	0.08	0.1078
Be	0 - 0.3	0.025	<0.0001
B	0.3 - 73	4.5	1.4552
Cd	0 - 0.19	0.0037	<0.0016
Cr	0 - 33.4	0.053	<0.0012
Cu	0 - 10	0.024	<0.0012
Fe	0.2 -5500	24.0	<0.0006
Pb	0 - 5.0	0.054	<0.023
Mn	0.06-1400	0.6	<0.0003
Mo	0 - 0.52	0.013	<0.0034
Ni	0.01- 0.8	0.069	<0.0068
V	0 - 1.4	**	<0.0008
Zn	0 -1000	0.5	0.0239

** not determined
(after Daniel and Liljestrand (1984))

Only one sample of leachate was submitted for ICP-AES analysis. This was obtained from the gatehouse well at the Mountain Road landfill site. Concentrations of the trace constituents manganese, molybdenum, aluminum, nickel, lead, cobalt, chromium, copper, cadmium, beryllium, antimony, and vanadium were all found to be below ICP determination limits. The trace constituents present in measurable concentrations were boron, arsenic, phosphorous, zinc, iron, and barium. Data presented by Daniel and Liljestrand (1984) shown here in Table 5.4, indicates that a wide range in the concentration of trace constituents is possible in landfill leachates. A comparison of trace element data for the landfill leachate in this study with the data presented in Table 5.4 suggests that the Mountain Road leachate concentrations are comparable to the lower range of concentrations given.

5.3.5 Summary

The characteristic features of the major, minor and trace element chemistry of the four potential contaminants are summarized in Tables 5.5a and 5.5b. Since these contaminants will undergo various degrees of dilution when mixed with groundwater, these summary tables emphasise chemical ratios in preference to absolute concentrations.

Table 5.5a Summary of distinquishing chemical features of road salts and fertilizers

POTENTIAL CONTAMINANTS	MAJOR ION CHEMISTRY	MINOR ION CHEMISTRY	TRACE ELEMENT CHEMISTRY
ROAD SALT	- chemically very pure, containing Na or Ca, Cl - Na/Ca = 10^{+3} - SO_4/Cl ratios = 10^{-3} - enriched in Cl relative to NO_3: Cl/NO_3 = 10^2 depleted in HCO_3 relative to NO_3	- depleted in I relative to seawater: I/Cl=10^{-6} - Br/Cl ratios = 10^{-5}	- measurable concentrations of: Ba, Cu, Fe, Al, Ni - all other trace constituents below ICP determination limits - depleted in Ba relative to Cu, Ni, and Fe
INORGANIC FERTILIZERS	- phosphate fertilizers highly enriched in Na: Na/Ca= 10^{+2} - nitrate fertilizers enriched in Na: Na/Ca= 10^0 - 10^{+1} - enriched in NO_3 relative to Cl: Cl/NO_3= 10^{-1} - enriched in HCO_3 relative to NO_3	- enriched in I relative to seawater: I/Cl= 10^{-4} - Br/Cl ratios: 10^{-2} - SO_4/Cl ratios: 10^{+2} for phosphate fertilizers - SO_4/Cl ratios: 10^0 for nitrate fertilizers	- phosphate fertilizers characterized by measurable concentrations of Mn, P, Mo, Al, Zn, Ni, Fe, Cu As, V, B, Ba, Be - phosphate fertilizers enriched in Mn relative to Zn - nitrate fertilizers characterized by elevated Pb concentrations relative to Cu - characterized by measurable concentrations of Pb, Cd, Se, Sb

Table 5.5b. Summary of distinguishing features of bedrock waters and landfill leachates

POTENTIAL CONTAMINANTS	MAJOR ION CHEMISTRY	MINOR ION CHEMISTRY	TRACE ELEMENT CHEMISTRY
HIGH CHLORIDE BEDROCK WATERS	- enriched in Cl relative to NO_3: $Cl/NO_3 = 10^{+3}$ and SO_4: $Cl/SO_4 = 10^{+2}$ - enriched in Na relative to Ca: $Na/Ca = 10^{+2}$	- enriched in I relative to seawater $I/Cl = 10^{-5}$ to 10^{-7}	- enriched in Mn relative to Zn - enriched in Sb relative to Ni, Fe, Cu, Ba - measurable concentrations of all trace elements
LOW CHLORIDE BEDROCK WATERS	- depleted in Na relative to Ca ($Na/Ca = 10^{-3}$) - $Cl/NO_3 = 10^{+1}$	- enriched in I relative to seawater $I/Cl = 10^{-4}$ - $SO_4/Cl = 10^0$	- measurable concentrations of Mn, Al, Zn, Ni, Fe, S, Ba, B
LANDFILL LEACHATES	- $Cl/NO_3 = 10^{+1}$ - highly enriched in HCO_3	- $I/Cl = 10^{-2}$	- measurable concentrations of P, Zn, Fe, S, As, B, Ba

5.4 Chemical character of the contaminants in the unsaturated zone

As indicated in Section 5.3.1, this part of the study was concerned primarily with the chemical changes contaminants undergo as they move from the surface into the saturated zone. It focused on two important non-point contaminants - road de-icers and fertilizers, chemicals which are dissolved by precipitation at the surface but become subject to considerable chemical change during subsurface migration. These reactions can involve adsorption, ion exchange, mixing and dilution and may completely modify the chemical character of the contaminant.

As discussed in Section 4.2.3., 7 sites were selected for this part of the study. These included urban road, snow dump, rural road, urban park, fallow field, and two cropland sites. Sediments from the unsaturated zone were sampled, and their interstitial waters were extracted and analyzed. For the purposes of description and discussion most of the relevant data are presented in this report in the form of chemical depth profiles. Profiles relevant to the discussion are contained in this section; others may be located in Appendix VII.

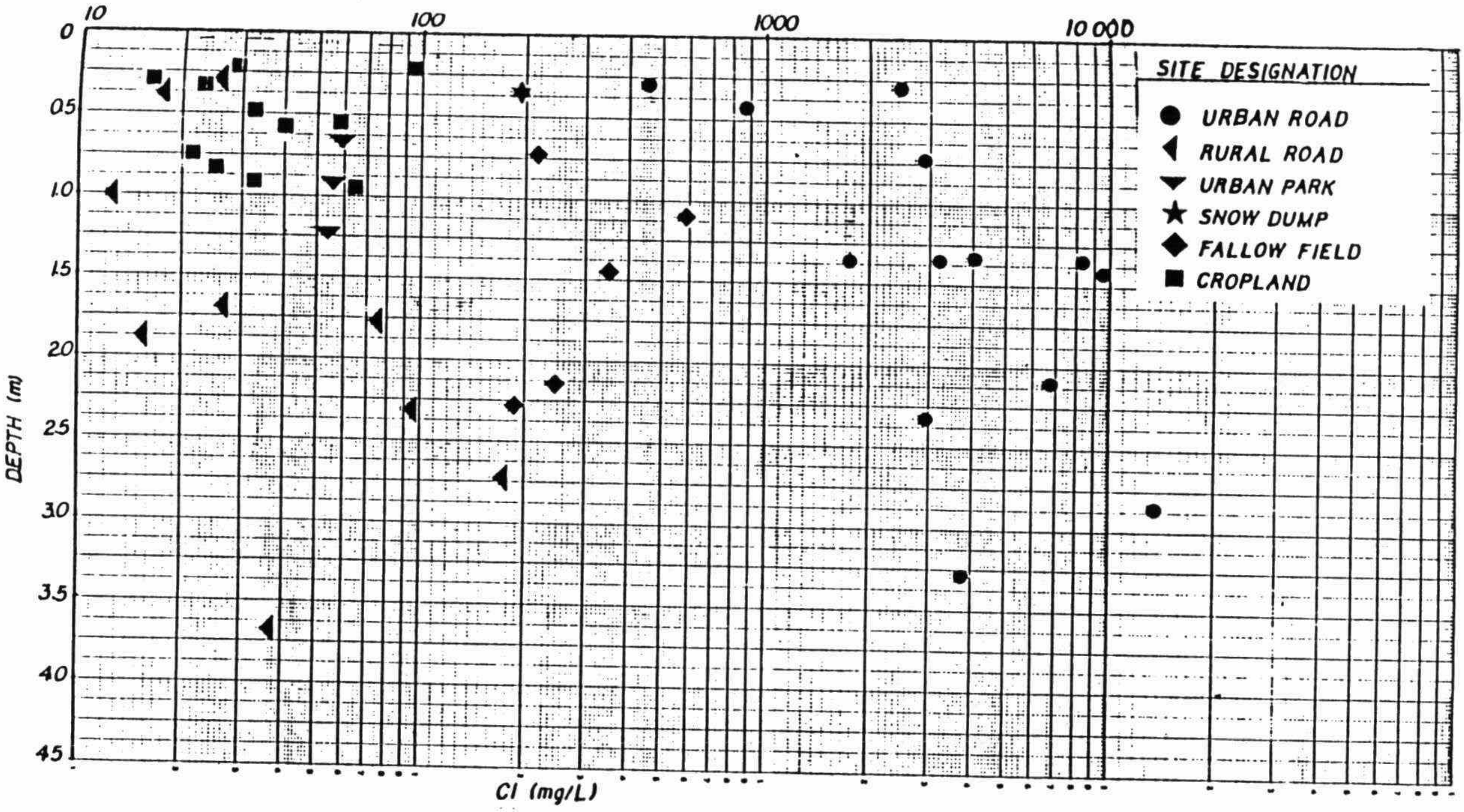


Figure 5.28 Plot of chloride concentration versus sample depth, interstitial waters

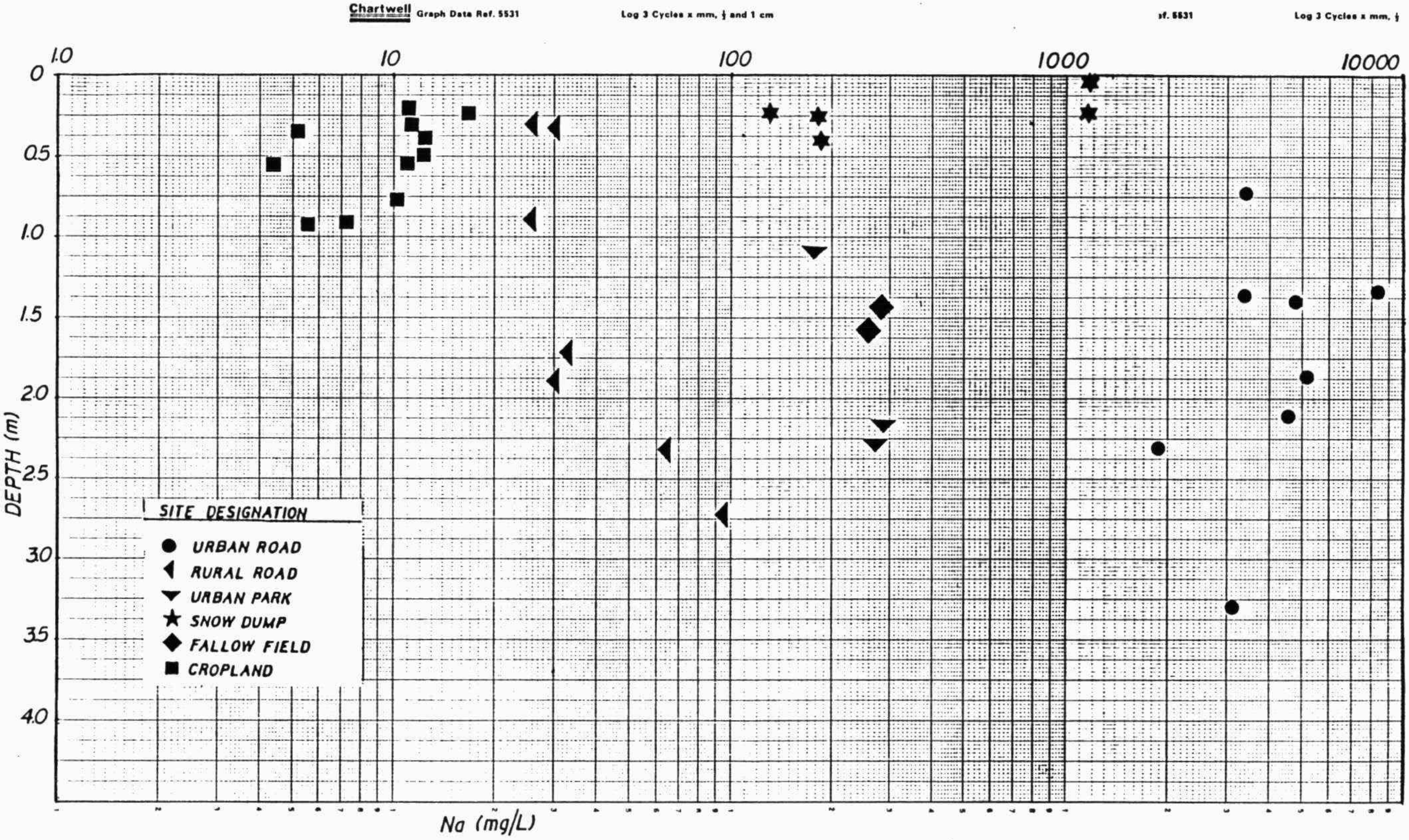


FIGURE 5.29 Plot of sodium concentration versus sample depth, interstitial waters

5.4.1 Urban road sites

Hydrochemical profiles at the urban road sites display considerably elevated concentrations of Na and Cl (Figures 5.28 and 5.29). Interstitial waters at these sites display chloride concentrations between 10^2 and 10^4 mg/L and sodium concentrations between 10^2 and 10^3 mg/L as compared with concentrations of 10^1 mg/L Cl and 10^1 mg/L Na for rural road sites. As shown by the figures, the zones of high salinity extend to depths in excess of 3.3m, and in some cases occur at distances as great as 100m from the road surface. The elevated Cl and Na concentrations are evidently associated with the large amounts of road de-icing chemicals (in Metropolitan Toronto exclusively NaCl) which are applied to the nearby Don Valley Parkway during the winter months.

The extensive zones of high salinity at the urban sites probably represent many years of exposure to road salt contamination. The pattern of increasing chloride concentration with depth may reflect differences in road salt loadings from year to year as well as differences in the amount of precipitation from one spring to the next. In a study by Toler and Pollock (1974), which covered a period of 4.5 years, it was noted that chloride concentrations were especially elevated during low rainfall seasons when volumes of water were insufficient to provide an adequate flushing of the shallow sub-surface.

A close examination of the depth profiles indicates that the chemical character of the infiltrating solutions is not maintained during its downward migration. At both the rural and urban road sites there is a general trend of slightly increasing chloride concentration with depth, while sodium concentration remains relatively constant with increasing depth. While a number of factors may be operating, ion exchange is thought to be the most important. In these reactions Na ions will be adsorbed onto colloid particles in exchange for the release of Ca ions according to the reaction:

$$2Na^{+} + Ca_{(ad)} = 2Na_{(ad)} + Ca^{2+} \qquad (2)$$

The effect of this process is to remove sodium ions from the soil solution, while calcium concentrations increase. Hydrochemical profiles appear to confirm this process; sodium concentrations are considerably lower than expected for the corresponding chloride concentrations, while calcium concentrations are elevated by chemically equivalent amounts (Figure 5.30). Laboratory studies carried out by Howard(1986) have demonstrated the postulated ion exchange process.

Urban road sites contaminated by road de-icing chemicals also contain elevated SO_4 concentrations ranging from 118.45 mg/L at a depth of 0.71m to 600 mg/L at a depth of 2.32m (Figure 5.31). These values are considerably above background concentrations and appear to be related to the salinity. However, since sulphate concentrations in road salt are normally very low (typically three orders of magnitude less than chloride) its presence is highly anomalous.

As shown previously in Section 5.3.4, road de-icing chemicals are depleted in iodide relative to seawater. Consequently, it might be expected that interstitial waters contaminated by road de-icing chemicals would show a similar trend. A plot of I/Cl ratios versus Cl for interstitial waters is shown in

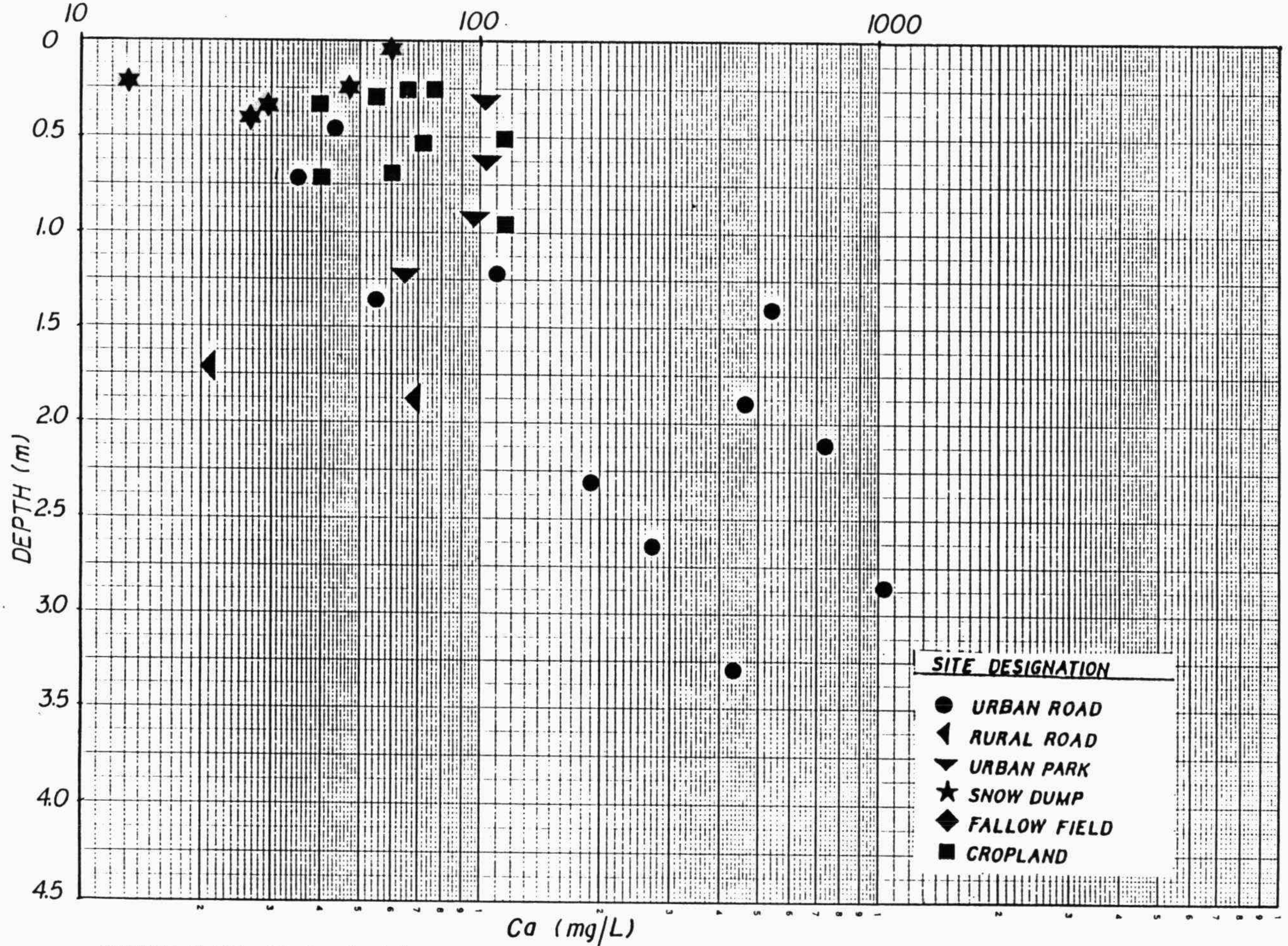


FIGURE 5.30 Plot of calcium concentration versus depth, interstitial waters

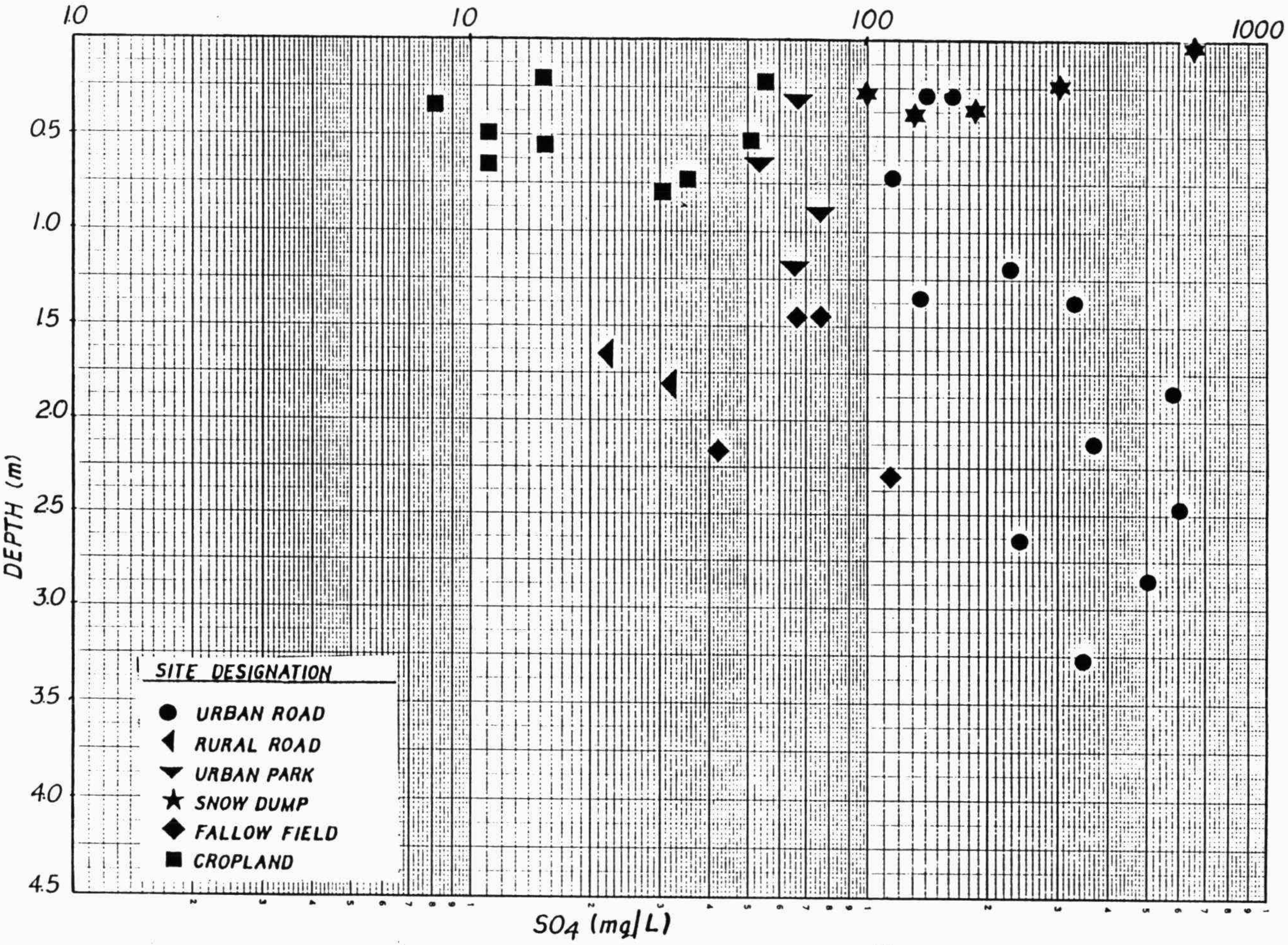
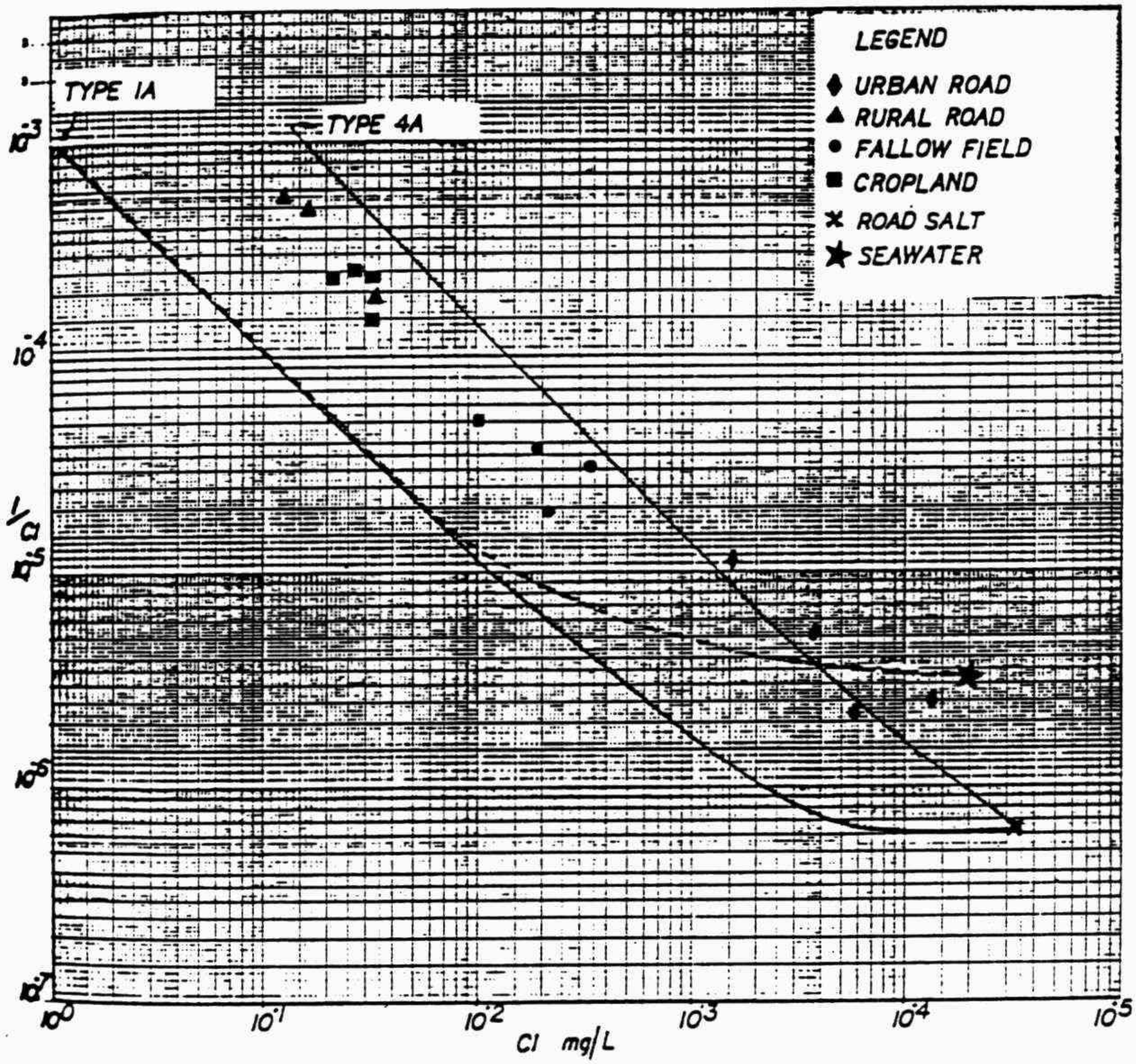


FIGURE 5.31 Plot of sulphate concentration versus depth, interstitial waters



5.32 Plot of I/Cl versus Cl for interstitial waters

Figure 5.32 together with three dilution curves. Two curves represent the mixing of Type 1A recharge waters with road salt (A) and seawater (B). A third curve represents the mixing of a high iodide fresh water (e.g.a Type 4A water) with road salt (C). The results are somewhat inconclusive in that the data appear to fit more closely with the upper, higher iodide dilution curve (Type 4A) when it would be more reasonable to expect that local uncontaminated groundwaters to be Type 1A in character. The results clearly illustrate the importance of knowing the background water chemistry of an area prior to its contamination.

As indicated in Table 5.2, road de-icing chemicals tend to be extremely pure, containing measurable concentrations of only five (Al, Ni, Fe, Cu and Ba) of the nineteen trace metals studied. Since the urban road sites are exposed to contamination from these de-icing chemicals it would not be unreasonable to expect that interstitial waters from the urban sites to display a similarly restricted range of trace elements. Certainly, Al, Fe, Cu and Ba were well represented in the interstitial waters beneath the urban road sites (Ni concentrations were consistently below the ICP determination limit); however, the urban road sites also exhibited enrichment in many other trace constituents which are less easy to explain. The trace constituent chemistry of the pore waters is discussed further below.

Trace element analysis of the interstitial waters obtained from road sites showed elevated concentrations of a wide range of trace metals. Barium, for example, an established constituent of road de-icing chemicals was found to occur at considerably elevated concentrations (up to 0.7 mg/L) (Figure 5.33). Of the other trace constituents of road de-icing chemicals , iron, aluminum, and copper (Figures 5.35, 5.36, and 5.38) were also found to be occur in elevated concentrations relative to the other sites, but their distributions were noticeably restricted to the upper 1 to 2 metres. Below this depth, these metals show a significant decrease in concentration which presumably reflects their relatively low mobility with a tendency to be adsorbed by the sediment matrix.

Other trace metals which appeared occasionally and usually in very shallow sub-surface waters include lead (up to 1.9 mg/L), molybdenum (0.07 mg/L (one sample)), chromium (up to 0.05 mg/L) and arsenic (0.13 mg/L (one sample)). Lead is a well documented contaminant from gasoline and diesel exhaust, (Scott, 1980; Garcia-Miragaya, 1984) and is usually emitted in the form of water soluble lead halides. Sources of the other trace metals are more speculative but they must presumably represent other urban pollutants.

5.4.2. Snow Dump Site

The interstitial waters sampled from the snow dump site exhibit considerable variability in trace constituent concentrations. Substantial enrichment in major, minor, and trace constituent chemistry was observed in Sample 8a collected from the centre of the site, while peripheral sites (20, 21, 22) showed only moderate to low enrichment. Sample 8a not only displayed major ion concentrations of the same order of magnitude as the urban road sites, it was significantly enriched in manganese (0.6 mg/L), phosphorous (2.4 mg/L),

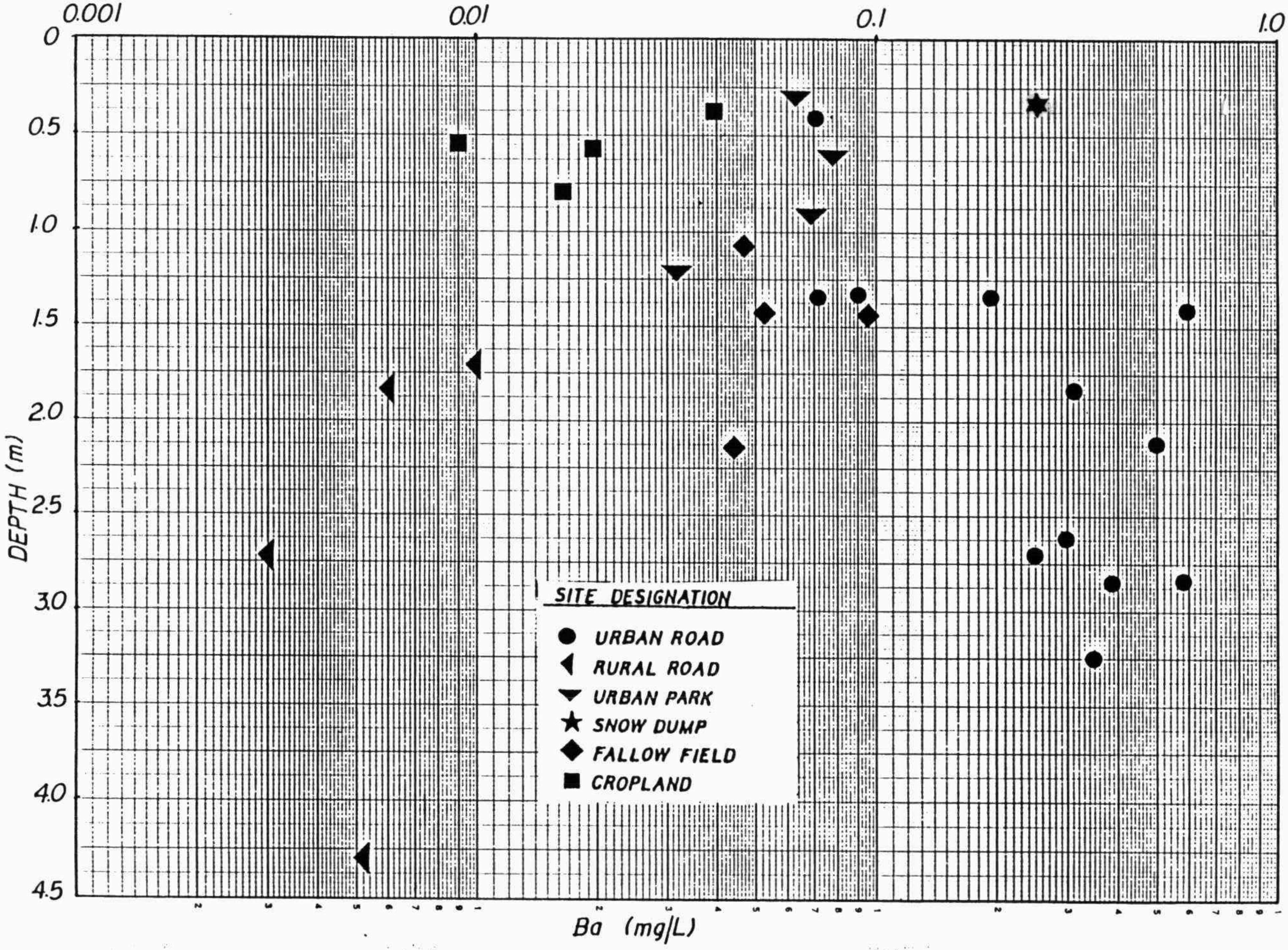


FIGURE 5.33 Plot of barium concentrations versus depth, interstitial waters

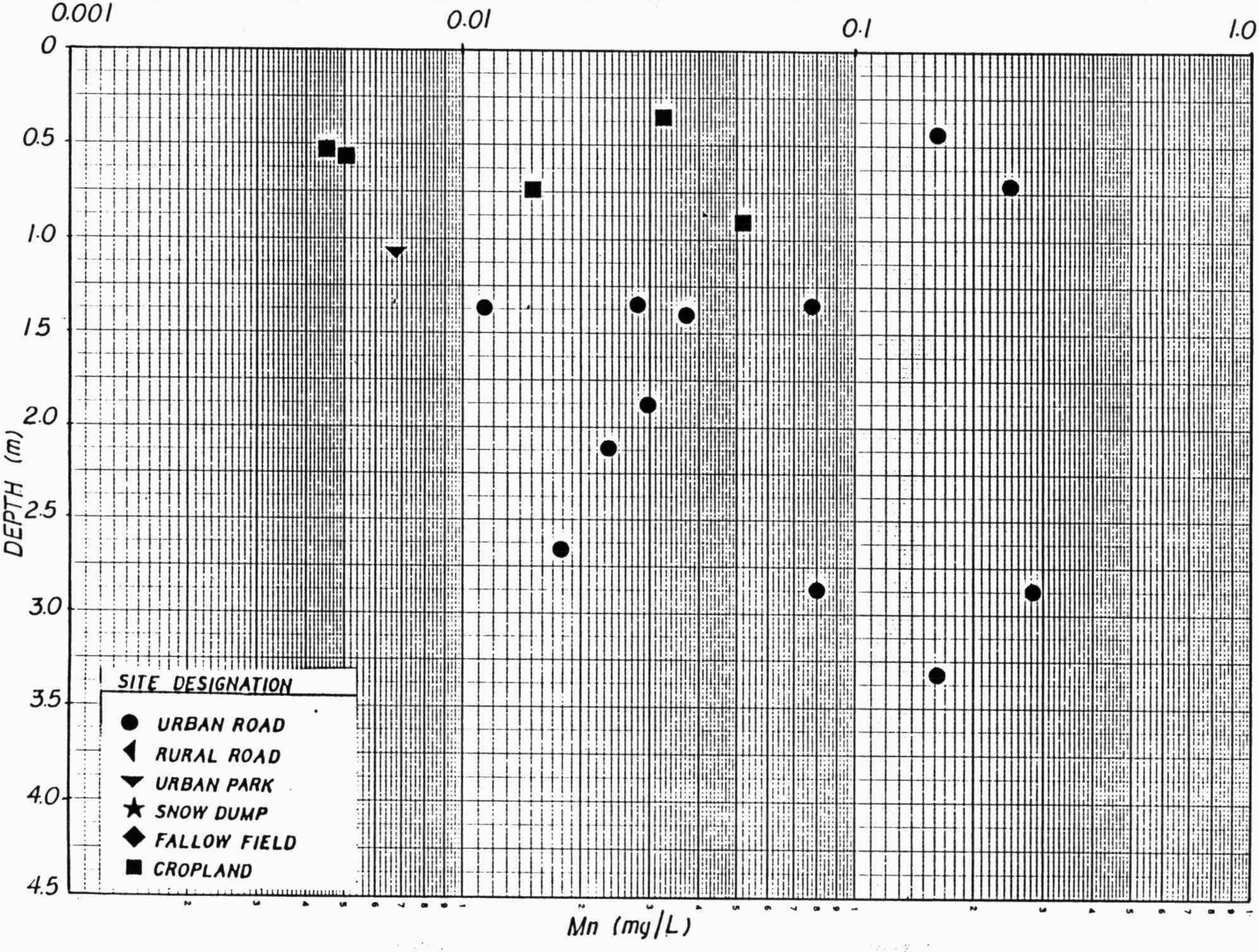


FIGURE 5.34 Plot of managanese concentrations versus depth, interstitial waters

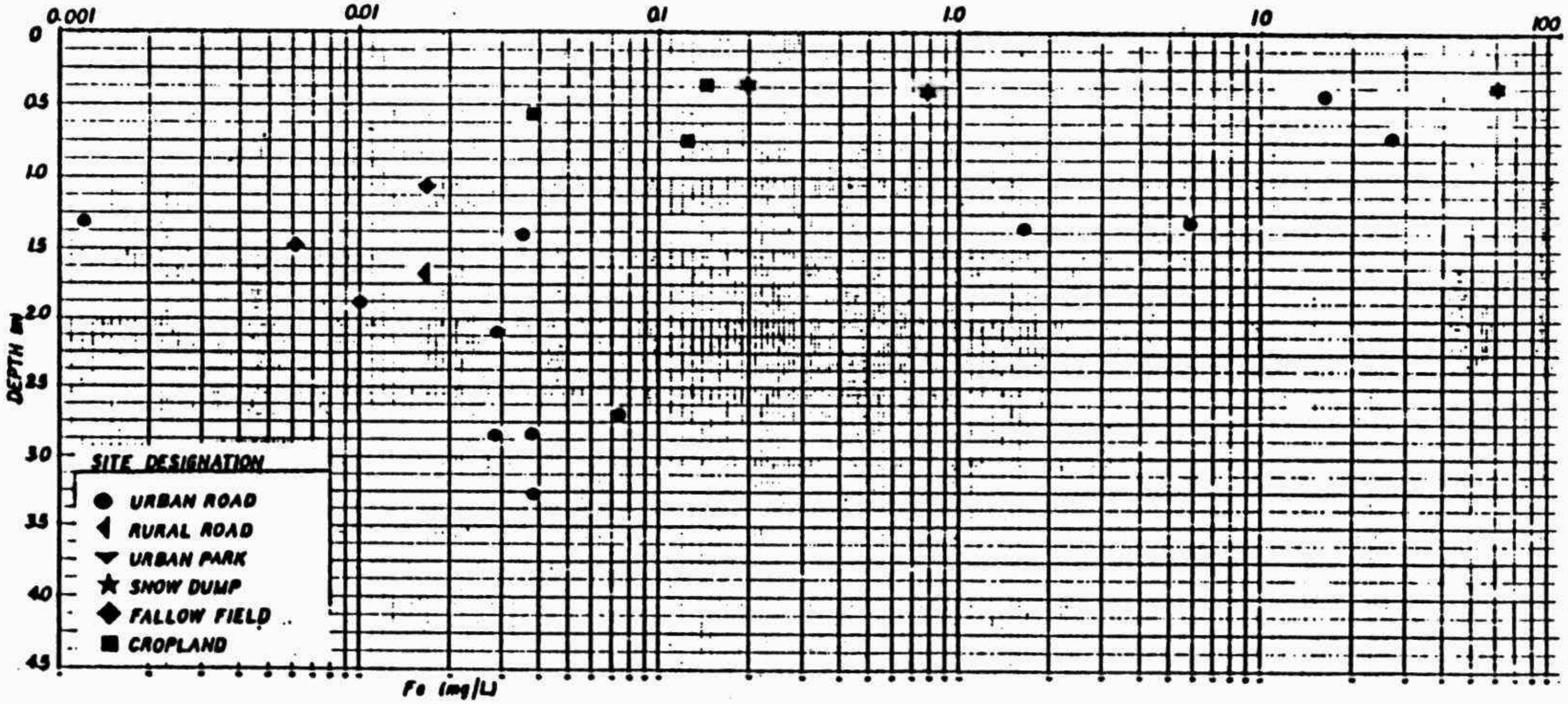


Figure 5.35 Plot of iron concentrations versus depth, interstitial waters

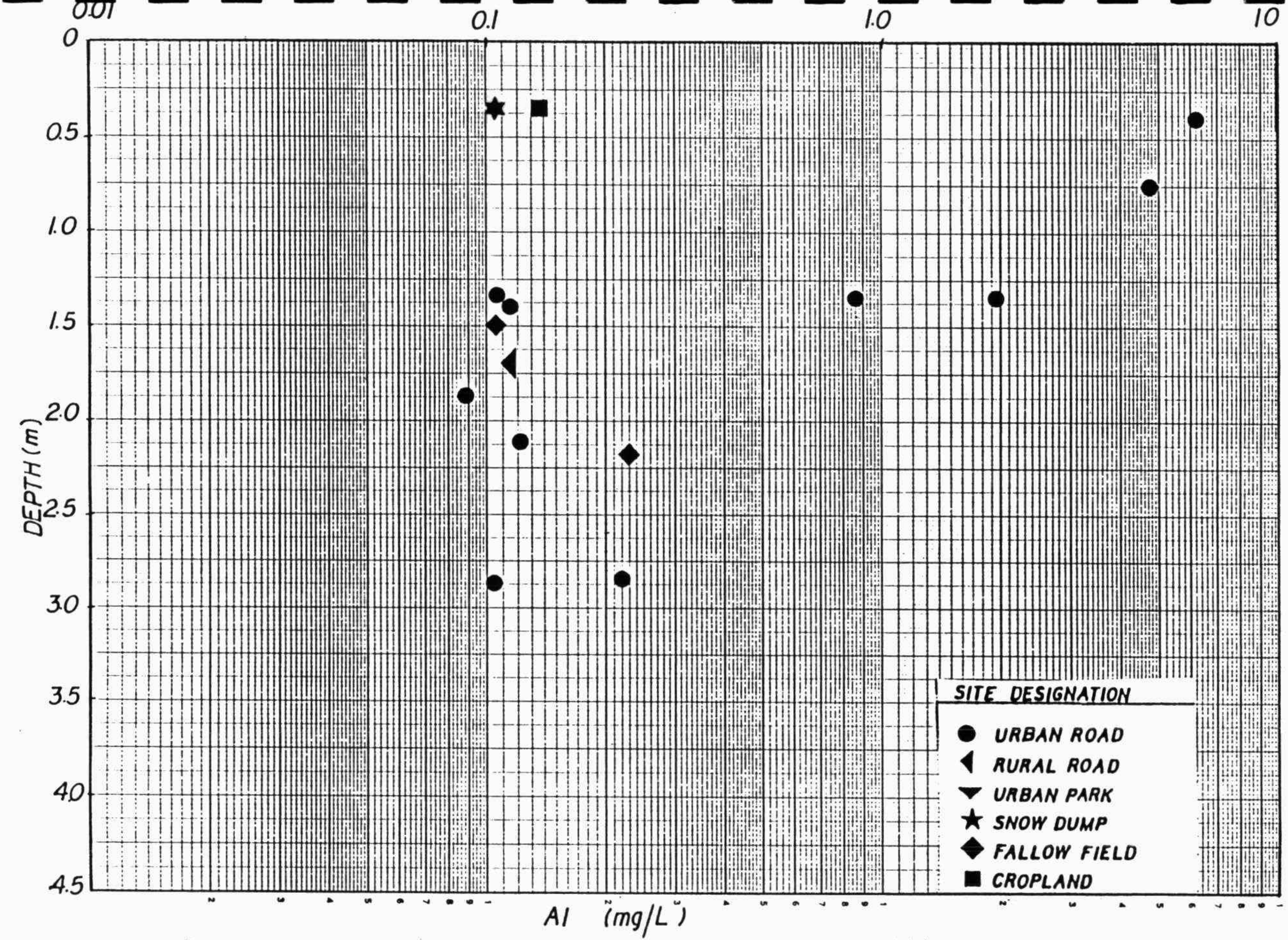


FIGURE 5.36 Plot of aluminum concentration versus depth

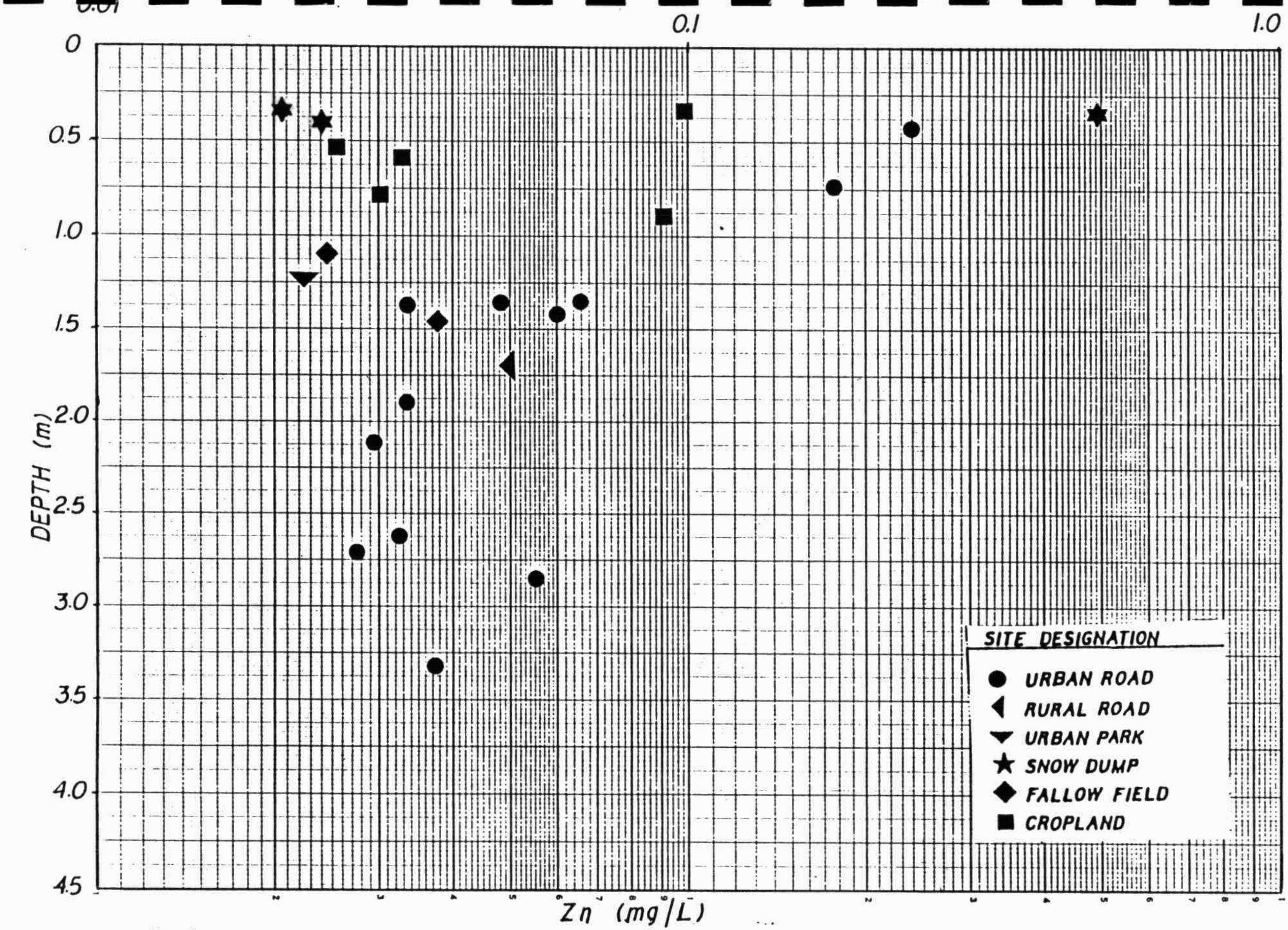


FIGURE 5.37 Plot of zinc concentrations versus depth, interstitial waters

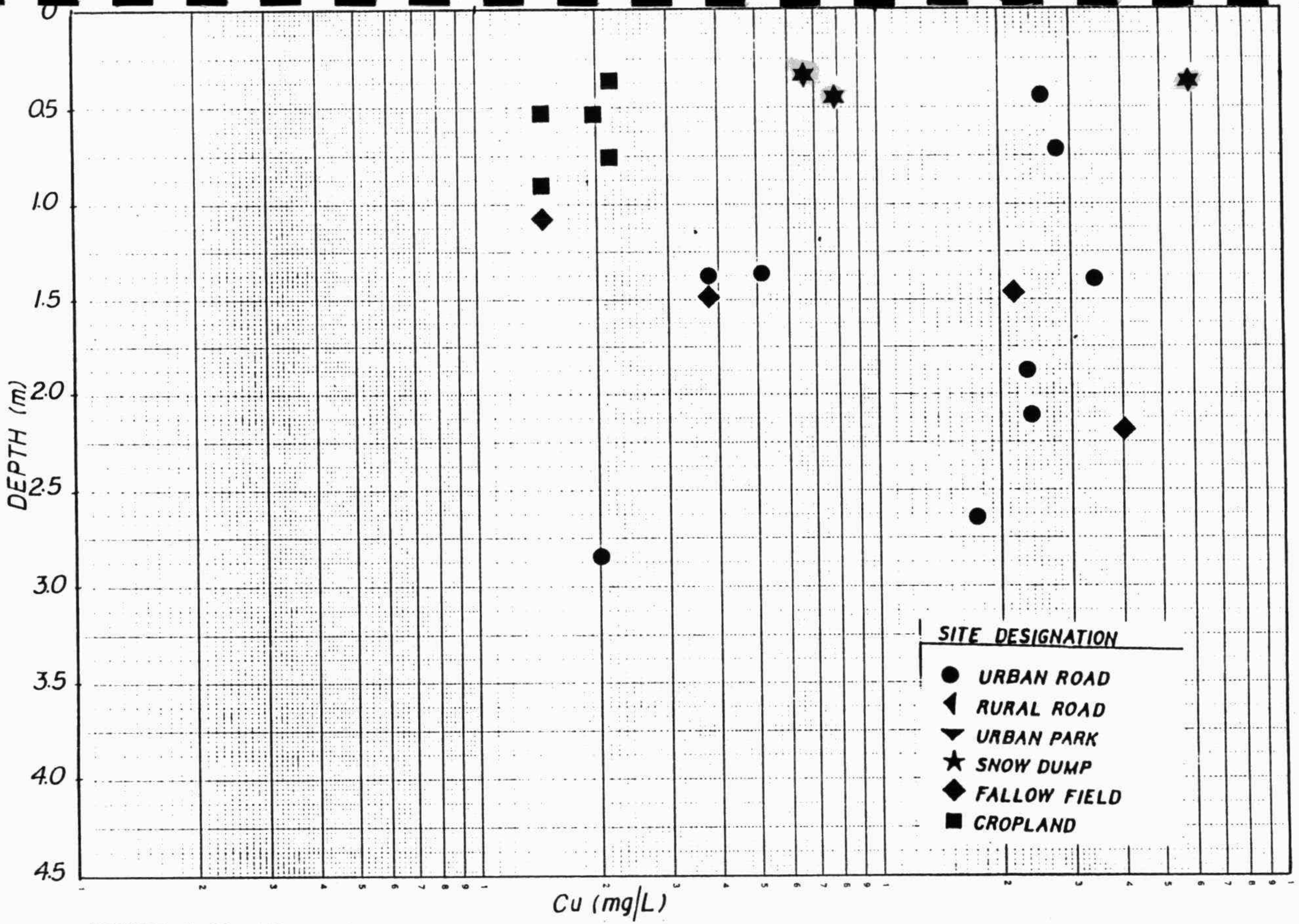


FIGURE 5.38 Plot of copper concentrations versus depth, interstitial waters

aluminum (17.8 mg/L), zinc (0.5 mg/L), iron (62 mg/L), lead (1.9 mg/L), copper (0.58 mg/L), chromium (0.07 mg/L), vanadium (0,14 mg/L), barium (0.25 mg/L), boron (0.23 mg/L) and beryllium (0.013 mg/L) relative to all other sites investigated.

It is believed that the unexpectedly high trace metal contamination beneath the snow dump site may be the result of accumulated particulate matter. When snow at the site melts it produces two sources of trace metal contamination: dissolved metals as might appear in run-off from salted urban roads, and particulate matter (urban dust) which although minor, will accumulate in large quantities as the dump continues to receive large quantities of snow. These particulates will tend to collect in the upper 30 cm of the soil column while the runoff solution infiltrates through this column into the unsaturated zone. Neutron activation analysis of sediments from the snow dump site (Table 5.6) confirms that soils from this site contain increased concentrations of certain elements (for example, chromium, iron, cobalt, and barium) in the solid phase relative to the urban road, rural road and cropland sites. The findings are corroborated by Scott (1980) who indicated that dumps receiving their snow from streets had a higher accumulation rate of sodium, chloride, and lead (the only constituents Scott (1980) studied) than those snow dumps receiving their snow from parking lot sites. It was also suggested by Scott (1980) that this difference was due to the higher amount of particulates in the street snow.

Table 5.6 Concentrations* of selected trace constituents in soils (ppm)

Site	Snow	Urban	Rural	Cropland	Range in soils**
V	30.0 - 60.0	30.0	30.0	30.0 - 80.0	20.0 - 500
Mn	20.0 - 200.0	50.0	40.0	50.0 - 100.0	100.0 - 4000
Cr	30.79- 40.29	26.2	20.89	23.11- 25.13	5.0 - 3000
Fe	2.15- 2.65	1.7	1.44	1.35- 2.20	+
Co	6.08- 8.71	5.05	4.39	5.17- 6.73	1.0 - 40
Ba	386.44- 490.83	377.50	394.38	243.75- 447.73	+
Ti	870.0 -1490.0	980.0	840.0	870.0 -4280.0	+

* analyzed by neutron activation
** from Rubin (1974)
+ not measured

5.4.3. Rural Road Sites

Rural roads generally receive considerably less road salt than their urban counterparts (36 kg/km c.f. 116 kg/km). Consequently, it is not surprising to find that, as shown by Figures 5.27 and 5.28, concentrations of chloride and sodium at the sites are two to three orders of magnitude lower than those of the urban road interstitial waters. The maximum chloride concentration observed was only 163 mg/L which, while considerably above background clearly represents considerable dilution by local fresh groundwater.

Trace metal concentrations in the interstitial waters are similarly low. Concentrations of chromium, cadmium, arsenic, nickel, lead, molybdenum, and cobalt in interstitial waters sampled from rural road sites are below ICP determination limits for these elements. Of the trace constituents normally found in road de-icing chemicals (Al, Ni, Fe, Cu and Ba), only Ba was regularly observed with Al, Fe and Cu appearing at detectable levels in only occasional samples.

5.4.4. Cropland and fallow field sites

Interstitial waters from the cropland and fallow field sites are low in total dissolved solids compared to urban road sites, but in comparison to uncontaminated Type 1A recharge waters, they display considerable enrichment in both nitrate and chloride. At the site near Brantford, chloride concentrations range from mg/L to mg/L and concentrations of nitrate range from 50 to 170 mg/L; at Milliken, chloride concentrations range from 180 to 585 mg/L and nitrates range from 40 to 300 mg/L.

Trace metal concentrations in interstitial waters from the cropland field sites are generally very low and are in most cases below ICP-AES detection limits. For example, of the trace constituents known to be present in inorganic fertilizers, concentrations of molybdenum, nickel, lead, cobalt, chromium, cadmium, arsenic, selenium, antimony, vanadium, and beryllium are all below ICP determination limits. While in part this may be explained by the limited mobility of most of these metals in soils, it should also be recognised that the nitrate fertilizers are diluted considerably by precipitation to form solutions that are about a hundred times more dilute than the .5% solutions analysed.

Not all of the trace ions present in the fertilizers are below ICP detection limits. Concentrations of manganese, barium, zinc, aluminum, phosphorous, copper, boron, and iron were present in measurable concentrations which is in contrast to the Type 1 uncontaminated recharge waters which, for example, do not contain any measurable concentrations of boron or, in many cases, aluminum. Phosphorous concentrations (Figure 5.40) were elevated (10^{-1} mg/L) in the upper 1 m of soil relative to the samples from the fallow field site (less than determination limit). However, the values are lower than observed at the urban road and snow dump sites. It should be noted from Figure 5.40 that phosphates show a decrease with depth, which reflects the tendency of phosphorous (in the anionic form of phosphate) to be strongly adsorbed in soils and undergo precipitation reactions as discussed in Section 3.3.3.4. In a study of anion mobility by Johnston et al. (1979), 98% of incoming phosphate was found to be retained in the upper 10 cm of the soil profile. Wiklander (1975) also maintains that phosphates are bound mainly in the upper part of the soil profile, and undergo very little leaching because they are so strongly adsorbed. Copper and boron are present in measurable quantities but their concentrations are only marginally above those expected in uncontaminated Type 1A waters (Figures 5.38 and 5.41). Boron is probably the more significant of the two elements. Aluminum is also present in elevated concentrations very close to the surface but is not detected at deeper sites.

Trace metal concentrations in the interstitial waters are similarly low. Concentrations of chromium, cadmium, arsenic, nickel, lead, molybdenum, and cobalt in interstitial waters sampled from rural road sites are below ICP determination limits for these elements. Of the trace constituents normally found in road de-icing chemicals (Al, Ni, Fe, Cu and Ba), only Ba was regularly observed with Al, Fe and Cu appearing at detectable levels in only occasional samples.

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Not all of the trace ions present in the fertilizers are below ICP detection limits. Concentrations of manganese, barium, zinc, aluminum, phosphorous, copper, boron, and iron were present in measurable concentrations which is in contrast to the Type 1 uncontaminated recharge waters which, for example, do not contain any measurable concentrations of boron or, in many cases, aluminum. Phosphorous concentrations (Figure 5.40) were elevated (10^{-1} mg/L) in the upper 1 m of soil relative to the samples from the fallow field site (less than determination limit). However, the values are lower than observed at the urban road and snow dump sites. It should be noted from Figure 5.40 that phosphates show a decrease with depth, which reflects the tendency of phosphorous (in the anionic form of phosphate) to be strongly adsorbed in soils and undergo precipitation reactions as discussed in Section 3.3.3.4. In a study of anion mobility by Johnston et al. (1979), 98% of incoming phosphate was found to be retained in the upper 10 cm of the soil profile. Wiklander (1975) also maintains that phosphates are bound mainly in the upper part of the soil profile, and undergo very little leaching because they are so strongly adsorbed. Copper and boron are present in measurable quantities but their concentrations are only marginally above those expected in uncontaminated Type 1A waters (Figures 5.38 and 5.41). Boron is probably the more significant of the two elements. Aluminum is also present in elevated concentrations very close to the surface but is not detected at deeper sites.

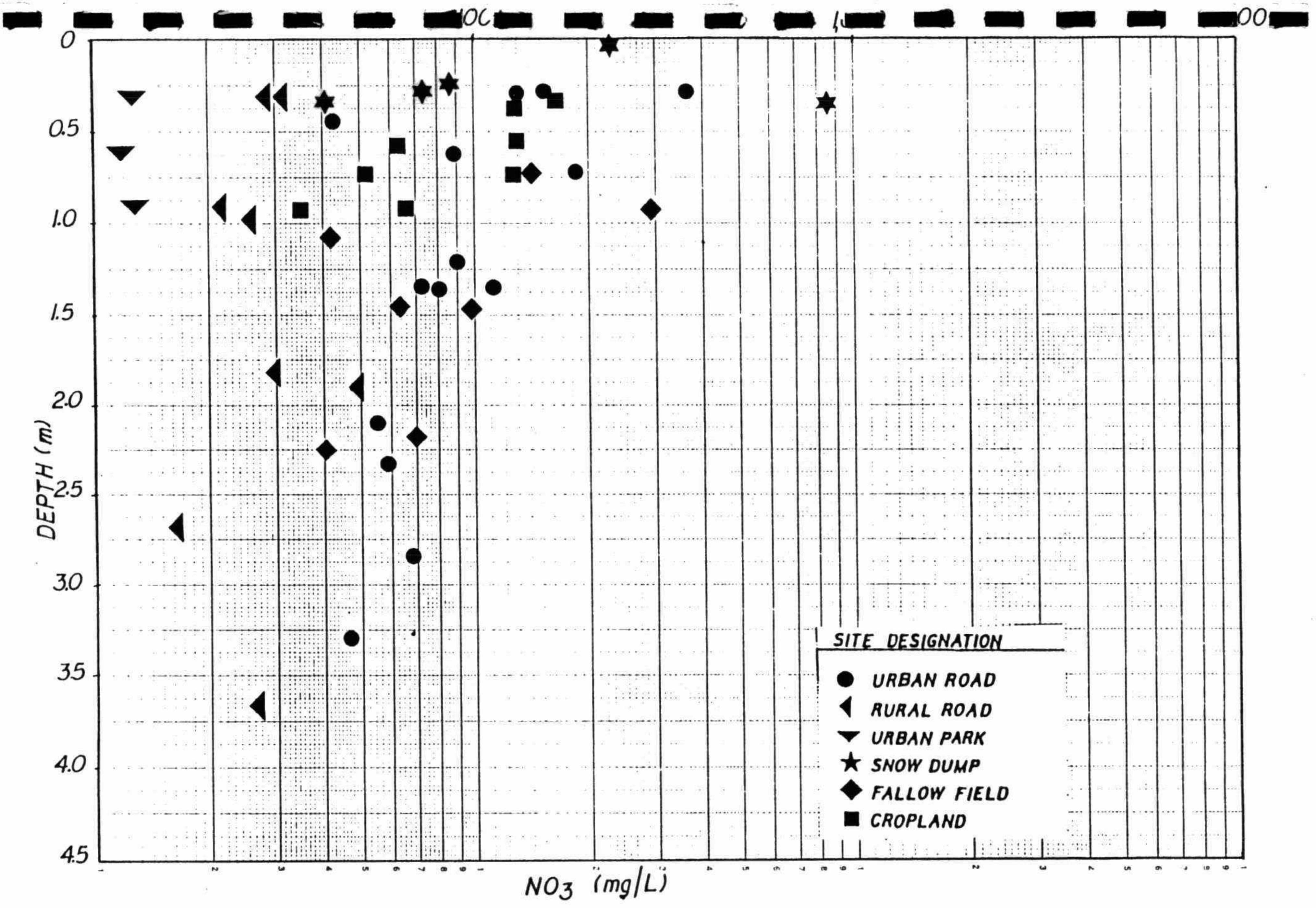

FIGURE 5.39 Plot of nitrate concentrations versus depth, interstitial waters

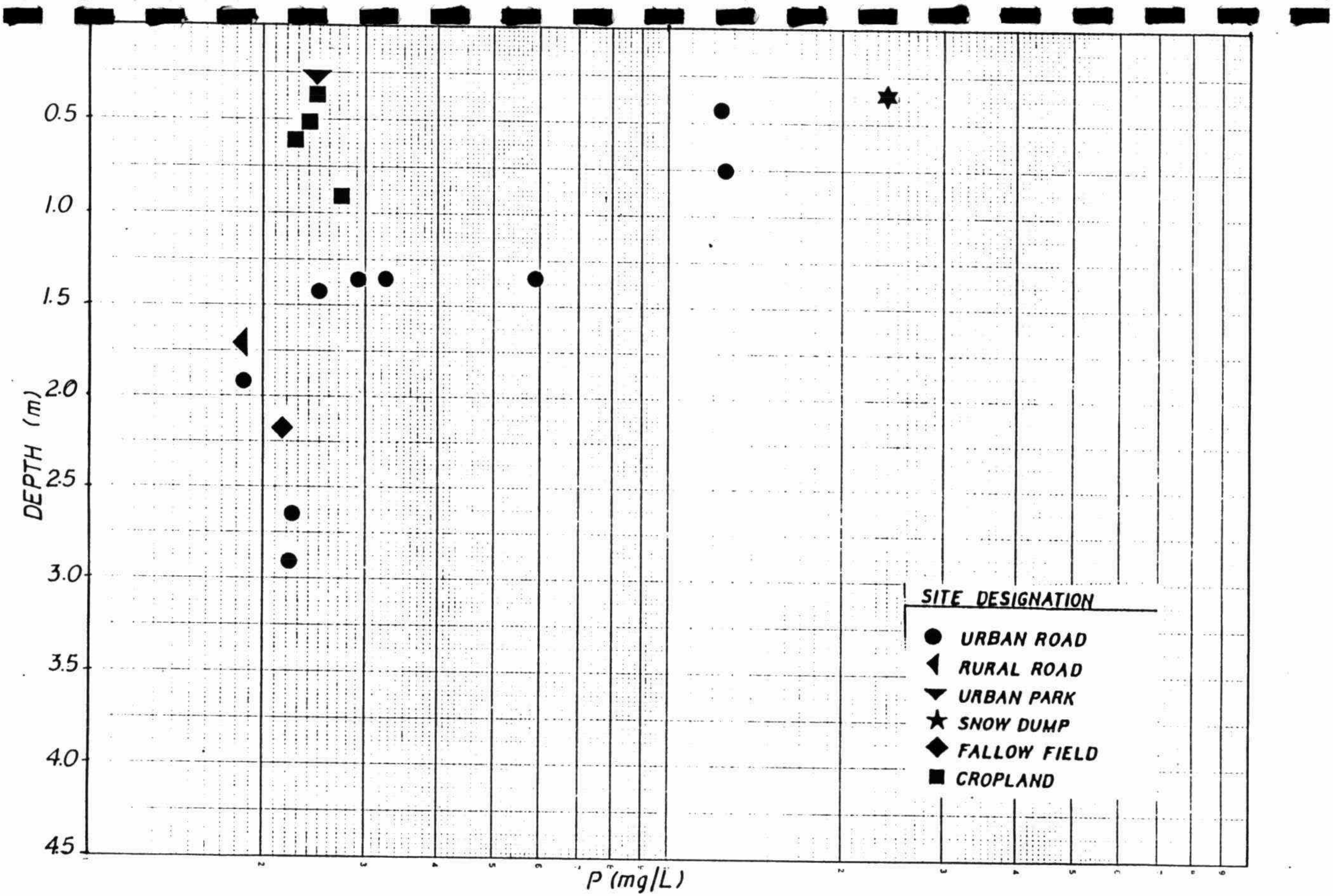

FIGURE 5.40 Plot of phosphorous concentrations versus depth, interstitial waters

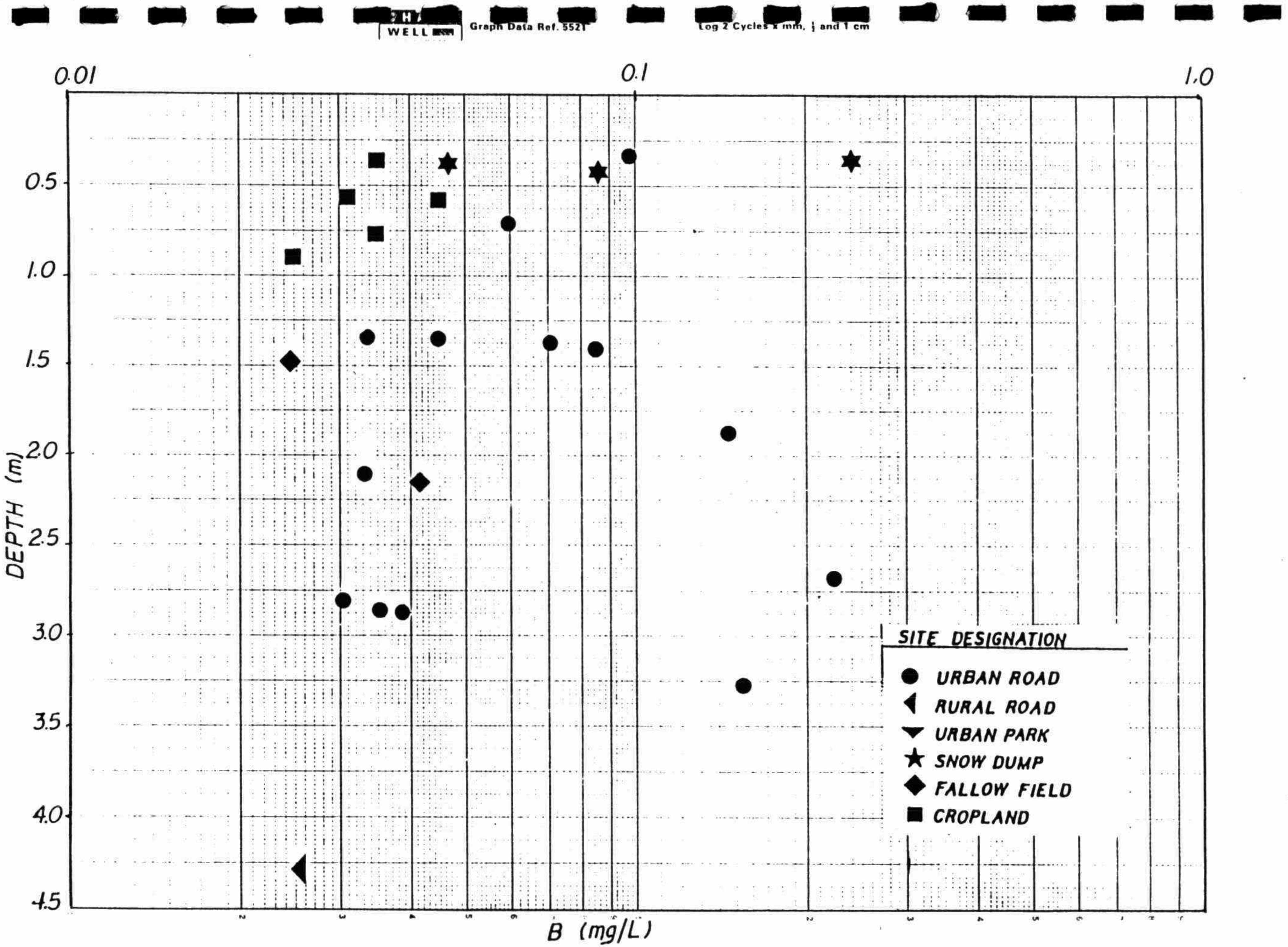

FIGURE 5.41 Plot of boron concentrations versus depth , interstitial waters

5.4.5 Summary

The interstitial water sampling program considered two non-point sources of chloride enrichment; road de-icing chemicals, and inorganic (and organic) fertilizers. At each of the sites, certain characteristics of the interstitial water chemistry were highlighted. It is important that these characteristics be examined in light of the chemical nature of the contaminants.

At urban road sites (Figure 4.3; Site A) concentrations of chloride, sodium, sulphate, calcium, barium, chromium, selenium and manganese were found to be present in elevated concentrations throughout the profile in comparison to other investigated sites. Iron, aluminum, zinc, copper were also present in elevated concentrations at shallow depths (above 1 - 2 m) but showed little difference to other sites, deeper in the profile. The elevated presence of barium, iron, aluminum, and copper can be associated with their presence as trace impurities in road salt (see Section 5.3.4). However, the presence of chromium, arsenic, molybdenum, lead and cadmium which were not detected in road de-icing chemicals, clearly reflect the influence of a diverse range of other urban pollutants.

Of the major ion constituents, chloride, sodium and calcium are the most important indicators of road salt contamination. The chloride is highly mobile, while sodium tends to undergo ion exchange with calcium. The presence of elevated calcium in groundwaters contaminated by NaCl road de-icing chemicals is a clear indicator that the contaminant has moved via a sub-surface route and has not simply leaked vertically into a poorly sealed well. From a trace constituent standpoint, road de-icing chemicals are remarkably pure, containing measurable concentrations of only nickel, iron, aluminum, barium and copper. Nickel appears to be immobile, and iron and aluminum are important constituents of soil and sediments. There are indications that copper and barium may be useful indicators of road salt contamination in certain situations. Also iodide appears to be useful, but only in situations where background concentrations of iodide are known to be low (< 0.005 mg/L).

Analysis of interstitial waters at fertilized cropland sites, indicate the presence of nitrate, calcium, phosphorous, boron, copper, zinc, manganese, and iron. While all of these chemical parameters are present to some extent in inorganic fertilizers, care must be exercised in interpretation, as concentrations of many of the trace element parameters are closely similar to natural background concentrations. Other than, of course, nitrate, only phosphorous and boron showed any potential as indicators of fertilizer contamination. Both these elements, however, have limited mobility and may be adsorbed under suitable conditions.

6. USE OF TRACE CONSTITUENTS TO IDENTIFY NON-POINT SOURCE CONTAMINATION OF GROUNDWATERS - A DISCUSSION

6.1 Introduction

To be useful as diagnostic indicators of contamination, chemical constituents should display certain attributes. According to Clark and Piskin (1976) these properties are as follows:

1) availability - the indicator should be present in distinguishing concentrations in the contaminant. The range of concentration is generally greater than that in uncontaminated groundwaters.

2) mobility - the indicator should be readily extractable from the contaminant and it should be mobile in a wide variety of soils. It should be capable of dissolving in the infiltrating precipitation;

3) chemically unreactive - the chemical parameter should be relatively unreactive and not undergo ion exchange, or sorption as it migrates through the unsaturated zone.

4) concentration - low concentrations of the chemical indicator should be present in uncontaminated groundwater in contrast to the chloride-enriching contaminant;

5) easily detected - the chemical parameter should be easily measured by field methods as well as a wide range of analytical techniques.

Few investigations have previously studied major, minor and/or trace constituent chemistry in an attempt to identify chemical indicators of specific contaminants. Beck and Howard (1986) suggested that I/Cl ratios may be used to distinguish between saline bedrock waters and road de-icing chemicals, while Clark and Piskin (1976) identified boron, iron, ammonia and total dissolved solids as useful indicators of landfill leachate contamination. The NO_3/Cl ratio has also been identified by Hill (1982) as a useful chemical indicator of groundwater contamination from fertilizers.

In the current study, the approach has been to measure the background levels of a large suite of chemical parameters in uncontaminated and contaminated groundwaters in the Duffins Creek-Rouge River basins. The large suite of chemical parameters provided a means of characterizing the groundwaters of the basin, with the result that anomalies due to contamination could be clearly identified. In particular, it was important to establish the chemical character of uncontaminated recharge (Type 1A) waters because it is these waters which are most prone to contamination. However, it was also necessary to document the changing chemical character of the groundwaters as they moved through the basin.

To identify potentially useful chemical source indicators of groundwater contamination, five well established groundwater contaminants were also chemically characterized using the same suite of parameters used for the groundwaters. Emphasis was placed on two groups of non-point source contaminants as outlined in previous sections (3.3 and 5.3.2). In an attempt to understand the extent to which the source contaminants are modified during sub-surface transport, site investigations were undertaken in areas believed to be affected by specific contaminant sources. These investigations focused on contamination by road de-icing chemicals and chemical fertilizers.

6.2 Discussion

6.2.1 Road de-icing chemicals

As shown in Section 5.3, road de-icing chemicals are chemically very pure, consisting mainly of sodium (or calcium in the case of $CaCl_2$) and chloride, together with minor amounts of sulphate, magnesium and calcium. The road salts also contain trace amounts of barium, copper, nickel, iron, and aluminum; all other trace elements were below ICP determination limits. Minor ion analyses showed the road salts to be depleted in iodide relative to seawater.

The interstitial water sampling program showed that many of the constituents present in road salt are mobile in the shallow subsurface. Such constituents include chloride, sodium, sulphate, calcium, and barium. Nickel appears to be immobile; copper, iron and aluminum have only limited mobility.

mobile

To identify possible chemical indicators of road salt contamination, groundwaters believed to be contaminated by road salt (Type 1S) were initially compared to uncontaminated recharge waters (Type 1A). Particular consideration was given (though not restricted to) those constituents which a) were identified in the source road de-icing materials and b) were found to be capable of migrating in the unsaturated zone (i.e. Ba, Cu, Fe, and Al). The following observations can be made:

1. Interstitial pore water studies suggested that aluminum and nickel which are present as trace impurities in road salts, have relatively low mobilities. Aluminum was measured in only the top 1 to 2 m of the soil/sediment profile adjacent to urban roads; nickel was not found at all. Their presence, therefore, in elevated concentrations in Type 1S waters deserves careful attention. The apparent anomaly is best explained by considering the detection limits of the analytical methods. It would appear that use of a pre-concentration technique to improve detection levels in the large groundwater samples reveals the presence of nickel and aluminum at concentrations which would not have been detected in the smaller pore water samples. In conclusion, it would appear that both aluminum and nickel have a potential use as indicators of road salt contamination provided adequate analytical methods are available. Nickel shows perhaps more potential than aluminum, as analytical

data for older uncontaminated water Types 2A through 4A which show significant concentrations of aluminum that are presumably naturally derived from the sediments.

2. Measurable concentrations of arsenic and antimony are exclusive to the contaminated Type 1 (1U, 1S, 1N) waters, and are not present in Types 1A, and 2A through 4A. The presence of arsenic and antimony in the Type 1S waters is unexpected as these elements are not present in road salt at source. However, these elements are present in albeit low concentrations in inorganic fertilizers such as ammonium nitrate, and it is possible that some waters classified as Type 1S, particularly in fertilized areas are contaminated in this way.

3. Boron is another example of an element which is not detected in road salt at source, but occurs in waters classified as Type 1S. It also becomes elevated in water Types 2A through 4A waters relative to all Type 1 waters. Boron has a wide variety of industrial and agricultural uses, and its presence in Type 1S waters is a useful illustration of the way in which waters susceptible to pollution (perhaps due to shallow depth and urban location) are frequently contaminated by more than one chemical source.

4. Barium is one of five trace constituents of road salt that appears to be mobile in the unsaturated zone and which may have potential as an indicator of road salt contamination under suitable conditions. Figure 6.1 shows two dilution curves (A and B) representing the mixing and dilution of 5% road salt solutions, containing approximately 5 mg/L Ba, with Type 1A waters. The Type 1S waters plot close to these dilution lines, but since these waters represent relatively dilute solutions (Cl of the order of 100mg/L), the Ba concentrations in two of the three samples are not significantly different from concentrations observed in Type 1A waters. However, as indicated by the diagram, Ba may prove a significant indicator of road salt contamination at higher salinities on the proviso that its enrichment is not limited by solubility constraints. For example, most barium salts are relatively insoluble and high significant concentrations of sulphate and carbonate in particular may cause precipitation. High concentrations of sulphate in the unsaturated zone adjacent to urban roads would explain why urban road interstitial waters plot below the dilution curves in Figure 6.1. It should be noted that barium is also a significant component of saline bedrock waters.

5. Copper is also one of the few trace constituents of road salt that is relatively mobile in the unsaturated zone and is potentially useful as an indicator of road salt contamination. Unfortunately, copper is also a significant trace constituent of some phosphatic fertilizers; it also occurs in elevated concentrations in saline bedrock waters. Thus its use as an indicator element is somewhat limited.

6. Iodide/chloride ratios are probably the most reliable indicator of road salt contamination. Road de-icing chemicals are significantly depleted in iodide ($I/Cl = 10^{-7}$) relative to seawater ($I/Cl = 10^{-5}$) and

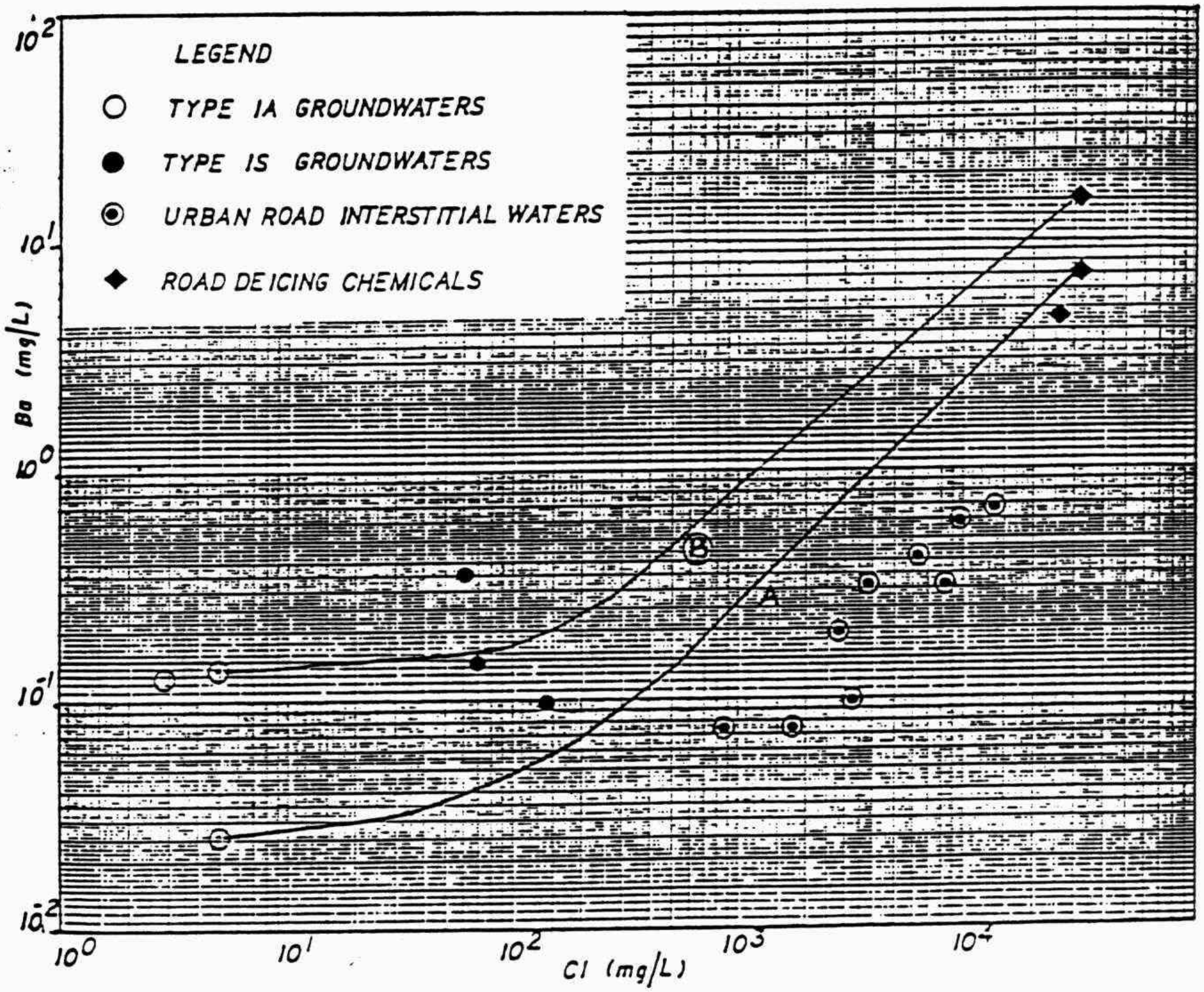

Figure 6.1 Plot of barium versus chloride

saline bedrock waters (10^{-2} to 10^{-4}). Provided that the issue is not confused by the dilution of low iodide road salt solutions with relatively high iodide fresh groundwaters, I/Cl ratios have considerable potential for diagnostic purposes, particularly when used and interpreted in combination with other indicator elements.

7. Many groundwaters contaminated by road salt show high Ca and relatively low Na concentrations, the result of ion exchange as the road salt pervades the aquifer. The presence of ion exchange indicates that the saline water is actively entering a region which has not previously experienced high Na waters. Consequently there are considerable amounts of calcium ions available at exchange sites. In general, saline bedrock waters tend to be more extensive and rapidly exhaust exchangeable calcium. Thus, unless saline bedrock waters are actively moving into parts of the aquifer which have had no previous experience of saline (high sodium) water, such waters tend to exhibit relatively low, more natural, Ca/Na ratios.

6.2.2 Inorganic fertilizers

Identifying potential chemical indicators of inorganic fertilizer contamination is more difficult due to very diverse chemical character of many of the fertilizers currently in use. As discussed in Chapter 5, inorganic fertilizers are characterized by different suites of major, minor and trace element constituents depending on the crop type and potential soil deficiencies. In many cases different fertilizers are applied each year, a consequence being that some pore waters underlying agricultural land may exhibit an usually large range of trace chemicals.

To identify possible chemical indicators of inorganic fertilizer contamination, groundwaters believed to be contaminated by fertilizers (Type 1N) were compared to uncontaminated recharge waters (Type 1A). As in the case of road salt, particular consideration was given (though not restricted to) those constituents which a) were identified in the source fertilizer materials and b) were found to be capable of migrating in the unsaturated zone (i.e. ionic constituents and B, Mn, Cu, Fe, and Zn). However, some consideration was also given to apparently less mobile constituents as it was recognized that such constituents could be mobile at sites more sandy (less clay rich) than that investigated.

1. In general, and as be would expected, the two primary types of fertilizer - phosphate fertilizers (mono- and di- ammonium phosphate) and nitrogen fertilizers are clearly distinguishable by the respective presence of phosphate and nitrate. Phosphate fertilizers also show elevated concentrations of iodide. Elevated nitrate concentrations are commonly observed at sites contaminated by nitrogen fertilizers; phosphates, on the other hand, tend to be considerably less mobile and much less commonly observed in sub-surface waters.

2. Unlike road de-icing chemicals which exhibit a very limited range of trace chemical constituents, fertilizers appear to contain an extraordinary wide range of chemicals including the more exotic elements such as antimony and arsenic. Significantly elevated arsenic and antimony concentrations were observed at several well water sampling sites. In fact the enrichment in arsenic and antimony appears to be restricted entirely to waters classified as contaminated Types 1S, 1N, and 1U. It is further noted that the interstitial water sampling program did not indicate the presence of arsenic and antimony. This is possibly explained by the clayey soils of the cropland sites which would likely have immobilized these elements. Sandy soils which prevail along the Oak Ridges of the Duffins Creek-Rouge River drainage basins are less likely to inhibit trace metal migration.

3. Boron is one of the more important trace constituents of fertilizer. It is also, however, present in domestic sewage and a wide range of industrial products. Boron was not detected in uncontaminated Type 1A waters, but was identified in Type 1N waters beneath the sandy soils of the Oak Ridges. While the origin of the boron in these waters would appear to be anthropogenic, its source must remain speculative.

4. Two other trace fertilizer constituents, zinc and manganese, were found to be mobile in the unsaturated zone, being present in the subsurface at the cropland site. Unfortunately, both zinc and manganese occur naturally in groundwaters and no significant differences are evident between the Type 1A and the contaminated Type 1N waters.

5. Many of the contaminated Type 1 waters which were classified by Beck (1985) as undifferentiated (Type 1U) showed measurable concentrations of nickel and aluminum. While their presence may be associated with road salt contamination as discussed in Section 6.2.1., it is noted that nickel and aluminum are also present in significant amounts in ammonium nitrate and both phosphate fertilizers. Nickel is particularly interesting in this regard as it is not usually present in uncontaminated Type 1A groundwaters.

7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusion

At the outset to the study, three objectives were set:

1) To determine the natural background levels of major ions (Ca, Na, Mg, K, HCO_3, Cl, NO_3, and SO_4), minor ions (I, F, Br) and trace metals (Mn, P, Al, Fe, Ba, B, Cd, Cr, Co, Se, Sb, As, V, Zn) in uncontaminated, naturally evolving groundwaters in shallow, surficial sediments.

2) To characterize potential contaminant sources by means of major ion, minor ion and trace metal parameters, in order to identify constituents which may prove diagnostic indicators of contaminant source.

3) To confirm that non-point source contaminants are accumulating in the shallow sub-surface, and to develop, through a knowledge of their sub-surface chemical character, a convenient and definitive hydrochemical method of identifying the contaminant origins.

It is clear that while considerable progress has been made towards all three objectives,. there exists no simple, definitive chemical means of identifying sources of low level groundwater contamination. This does not imply that inorganic chemical parameters do not have a role to play in source identification. It does mean, however, that inorganic chemistry must be interpreted carefully and selectively with due consideration to the degree of dilution, background hydrochemistry and the influence of chemical solubility and processes such as ion exchange.

The following summary examines the conclusions as they relate to each of the objectives listed above.

7.1.1 Background hydrochemistry

The importance of understanding the background geochemistry of the groundwaters is amply demonstrated by the study. Since most cases of groundwater contamination involve considerable dilution of the contaminant, the chemical characteristics of the resulting solution is clearly dominated by the chemistry of the original groundwater. The situation is further complicated by the realisation that groundwater chemistry is not constant, but changes naturally due to rock-water interactions as it moves through the system.

During the study , background levels of major, minor, and trace constituents were established for naturally evolving uncontaminated groundwaters in the Duffins Creek-Rouge River basins. It was shown that the distribution of many trace and minor constituents (e.g. Ba, Cu, Fe, Al, Mn, V, I) in the basins are closely related to the distribution of major ion groundwater types suggesting that the concentrations of these constituents are primarily controlled by natural chemical evolutionary processes and are minimally influenced by contamination. In contrast, the apparently random distributions of other trace constituents (e.g. As, Ni, Sb, Cr, Pb, Mo) indicate more local influences and are presumably related to contamination. It is clear from the regional study, that while very few (if any) sites in the Duffins Creek - Rouge River drainage basins can be classified as "polluted" (i.e. contaminated to the extent that water quality guidelines are exceeded), the majority do contain several constituents at concentrations that are above natural background levels.

7.1.2 Potential contaminant sources

The chemical compositions of the more important sources of chloride enrichment have been clearly documented. These sources include road de-icing chemicals, fertilizers, leachates, animal manures and bedrock waters. In each case over thirty chemical parameters have been determined.

The most important finding in this part of the study is the high degree of chemical purity associated with the two primary source contaminants - road de-icing chemicals and fertilizers. The road de-icing chemicals ($NaCl$ and $CaCl_2$) were determined to consist of chloride and sodium (or calcium in the case of $CaCl_2$), together with sulphate and trace amounts of barium, copper, iron, aluminum, and nickel. No other trace metals were identified. When it is recognised that the road salt solutions analysed contained approximately 30,000 mg/L Cl and 20,000 mg/L Na, the levels of sulphate (200 mg/L) and the trace metals (between about 5 and 200 mg/L) appear insignificant. It should also be noted that the road de-icing chemicals contain extremely low levels of iodide to the extent that they are depleted in iodide relative to seawater.

The inorganic fertilizers show considerable variation in their chemical compositions, but again exhibit unusually high purity with regard to their primary components. For example the 10% solutions of fertilizer analysed contained close to 100,000 mg/L of the primary components (e.g. nitrate, phosphate, ammonium ions) but typically contained less than 3000 mg/l sulphate, less than 100 mg/l sodium, and with the exception of aluminum (7 mg/L), less than 1 mg/L of each of the trace metals.

With regard to the other potential non-point sources of chloride, the highly saline bedrock waters also tend to be extremely pure with trace metals in the 1 - 20 mg/L range, even though chlorides reach nearly 300,000 mg/L. In most cases, the bedrock waters also exhibit a relatively high iodide concentration, thus distinguishing them from road de-icing chemicals. High iodide is also a character of local low salinity bedrock waters (Cl of the order of 100 mg/L).

7.1.3 Contaminant source indicators

The interstitial water sampling program focused on the behaviour of two non-point sources of chloride enrichment: road de-icing chemicals and inorganic (and organic) fertilizers. Close consideration was also given to bedrock waters as they can represent an important non-point source of contamination in specific areas.

The study confirms that non-point contamination of shallow groundwaters by chloride sources is an extensive problem. In the Duffins Creek - Rouge River drainage basins, the considerable majority of groundwaters sampled contained chloride in excess of 5 to 15 mg/L, the range of concentration which is estimated to represent background in naturally evolving uncontaminated groundwaters. Considerably elevated chloride concentrations were found in pore waters at all (over 20) auger sites. This includes the "fallow field site" selected initially as a control site, where chloride concentrations of several hundred mg/L were recorded.

Conclusive identification of contaminant sources was found to be more difficult. The recognition of suitable source indicators is complicated by four factors:

1) Source geochemistry - All the non-point sources investigated were found to be unusually pure with very few, if any, potential diagnostic indicators (see Section 7.1.2).

2) Dilution - levels of contamination in most of groundwaters investigated were extremely low; very few showed chloride concentrations in excess of 100 mg/L chloride. In many cases this represents a dilution of the contaminant of at least 100 to 1. Potential chemical source indicators are similarly diluted.

3) Mixing of contaminants - The wide range of trace elements measured in elevated concentrations both in the groundwaters and in the interstitial waters show that many sites are contaminated by more than one chloride source. This is especially true in urban areas where interstitial pore waters revealed, in addition to NaCl, extremely high sulphate concentrations (not present in road de-icing chemicals) and elevated concentrations of several of the more exotic heavy metals.

4) Soil geochemistry - The interstitial pore water studies indicate that the mobility of many of the trace elements are controlled by soil and sediment geochemistry. In urban areas elevated concentrations of several trace metals were limited to the upper 1 to 2 m of the soil profile; nickel was not detected at all. It is clear that the use of some diagnostic source indicators may be limited to soils and sediments which do not inhibit their migration.

Despite these difficulties, there remain several chemical parameters which can provide useful diagnostic information on sources providing conditions are suitable. For most (though not all) of these potential diagnostic indicators, these conditions include

a) the background chemistry of the water is well known;
b) the soils are relatively sandy and generally free of clays and hydrous oxides of iron and manganese which may inhibit trace metal migration;
c) contamination is well established and not excessively diluted.

Given these constraints, the trace element geochemistry of the source materials can provide a distinctive signature to the resulting contamination. For example, in the case of road de-icing chemicals the trace impurities appear to be strictly limited to barium, copper, iron, aluminum and nickel. On the understanding that the mobility of any of these metals may be impaired by local geological conditions, and that groundwater dilution may reduce the levels to insignificant concentrations, the presence of any or all of these elements in association with high levels of chloride is probably a good indication of a road salt origin. If iodide data are available and background concentrations of iodide are low, then low iodide/chloride ratios would provide further confirmation of a road salt origin. The existence of elevated sulphate (not present to a large extent in road de-icing chemicals) or other trace metals, would be a reasonable indication that sources other than, or in addition to, road de-icing chemicals are responsible for the contamination. For example, the trace metals chromium, selenium, arsenic, molybdenum, lead, and cadmium were present in measurable concentrations at the urban road sites and presumably represent contamination by urban and industrial sources such as chemical manufacturing and automobiles. Also, the trace elements boron and zinc were detected in all the bedrock waters investigated and may prove useful indicators of these waters as a contaminant source. It should also be noted that most of the bedrock waters are considerably enriched in iodide, and therefore are usually distinguishable from road salts on this basis alone.

With regard to agricultural activities, the interstitial water studies at cropland sites known to have been exposed to contamination from inorganic fertilizers, have indicated that the principal constituents of fertilizers entering the subsurface are nitrate, calcium, sulphate, boron, copper, zinc, manganese, and iron. There are indications that the clayey soils of the sites investigated may have limited the mobility of many of the trace elements. As a result, it is thought that a larger suite of potential indicators of fertilizer contamination may be available in areas of sandy soil. These indicators include nickel, aluminum, antimony and arsenic, all of which were found in contaminated groundwaters (1U and 1N).

7.2 Recommendations for further work

Based on conclusions reached in this study, it is recommended that further work be focused in the following areas:

1) Acid rain

It is suspected that a number of unexpected elements observed in the interstitial water sampling program may have been released from the soils and sediments by acid rain. Studies in northern Europe have indicated that acid rain can significantly alter the chemistry of the groundwater. Since a knowledge of background chemistry is essential if contaminant sources are to be identified, it is important that the effects of acid rain on groundwater quality be quantified.

2) Column studies

While the interstitial water sampling was generally successful, interpretation of the data was severely complicated due to the obvious presence of more than one contaminant at virtually all the sites investigated. To clarify a number of the findings, it is strongly recommended that further work be undertaken to study the soil-water interactions of specific contaminants. Ideally this would be carried out using field installed soil columns.

3) Geochemical modeling

The study has provided an extensive data base which would benefit from further analysis using geochemical modeling techniques. This approach would permit a closer evaluation of the trace element solubility constraints and the importance of rock-water reactions.

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APPENDIX I- ANALYTICAL METHODS

I.1 Introduction

Well water samples were analyzed for pH, the major ions Na, Ca, Mg, NO_3, HCO_3, SO_4, Cl; the minor ions K, CO_3, I, F, Br; and the trace constituents Mn, P, Mo, Al, Zn, Ni, Fe, Pb, Cu, Co, Cr, Cd, S, As, Se, Sb, V, B, Ba, and Be.

Interstitial pore water samples and contaminant samples were also analyzed for the same suite of major, minor and trace constituents where possible. However, some difficulties were encountered depending on the nature and volume of the sample. For example, many of the interstitial water samples were taken from unsaturated sediment, and in many cases, insufficient amounts of water were available for a complete analysis. Also, some of the contaminant samples were too turbid, despite repeated filtering, for analysis by colorimetry, inductively coupled plasma or atomic absorption or flame emission.

All major cations and minor anions were measured in the laboratories of the University of Toronto's Groundwater Research Group at Scarborough College; the trace constituents were measured at the University of Toronto's Inductively Coupled Plasma Laboratory at the Institute for Environmental Studies.

Towards the end of the study, it was decided to attempt elemental analysis of some of the sediment materials from selected auger locations. These were analyzed for minor and trace constituents at the University of Toronto's Slowpoke II Nuclear Reactor Facility.

This Appendix describes the analytical techniques adopted for the study. Some background theory is given for each analytical technique, and this is followed by a brief summary of the method applied to specific parameters and groups of parameters. Typical calibration curves will be shown where used. Appendices II, III, IV, and V provide the analytical results for the well water, interstitial water, contaminant and sediment sample suites respectively. The precision of the major cation and anion analyses is shown in Table I.1. Values of precision were determined using the relative standard deviation or coefficient of variation, according to the equation:

$$C_v = 100s/x \qquad (I.1)$$

where s is the standard deviation and x is the mean of n observations (American Public Health Association, 1985). For the values listed, calculations were based on 8 replicate sample analyses.

Table I.1 Summary of the analytical techniques for major cations and anions

Chemical Parameter	Analytical Method	Precision (%)
pH	Specific ion electrode potentiometry	0.2
NO_3	Specific ion electrode potentiometry	1.8
F	Specific ion electrode potentiometry	not determined
Cl	Specific ion electrode/	0.9
	Titration	not determined
HCO_3	Titration	0.02
SO_4	Turbidimetry/ Inductively coupled plasma	4.3
I	Colorimetry	0.07
Br	Colorimetry	0.7
Ca	Atomic absorption spectrometry/ Inductively couple plasma	0.4
Mg	Atomic absorption spectrometry/ Inductively coupled plasma	0.3
Na	Flame emission spectrometry	0.4
K	Flame emission spectrometry	1.2

I.2 Potentiometric Methods

Potentiometry is a water chemistry technique which is based on the relationship between the potential of an electrochemical cell and the concentration of the analyte. The method utilizes an ion selective electrode which responds to the concentration by changes in potential between a reference electrode which provides a constant half cell potential, and an ion meter to measure changes in voltage. The ion selective electrode is a membrane electrode which uses ions to carry current from the sample solution across the membrane to the reference solution (Midgley and Torrance, 1978). The result is that a change in potential develops across the membrane of the ion selective electrode that is related to the change in the analyte concentration (or more accurately, activity). Since the membrane potential cannot be measured, the difference in potential between the reference and the ion selective electrode is measured (Herman, 1981). The relationship between the potential and the analyte concentration is given by the Nernst equation,

$$E = E^{o} + 2.303\ RT/nF \log C \qquad (I.2)$$

where E_o is the reference potential, R is the gas constant, T is the absolute temperature, n is the number of electrons, F is the Faraday constant, and C is concentration of the ion.

All the potentiometric analyses described below were made using an appropriate ion selective electrode connected to either an Orion 407A Ion Analyzer or a Fisher Accumet Selective Ion Analyzer (Model 750).

I.2.1 pH

The pH of all the well water samples was measured in the laboratory within 6 hours of collection; the ph of contaminant samples and interstitial water samples was determined within 24 hours of collection. pH was measured using an Orion combination pH electrode (Cat. No. 91-05). The meter was calibrated using Fischer standard buffer solutions of pH 4, 7, and 10. The electrode was attached to an Orion Ionanalyzer or a Fischer Accumet Selective Ion Analyzer (Model 750).

Procedurally the analytical technique is very simple. The pH electrode is inserted into polyethylene tubes or vials containing 10 to 15 ml of sample, and stirred to ensure homogeneity. Measurements are taken when a stable reading is obtained, usually within one or two minutes.

I.2.2 Chloride

Two methods were used to measure chloride concentrations. One method involved titration and is discussed under the volumetric methods section. The second method was a direct measurement method using an Orion model 94-17 combination electrode filled with Orion 90-00-17 solution and attached to the Fischer Ion Analyzer (Model 750). For this method the chloride electrode was calibrated using 10, 100, 1000 ppm standards. To conduct the analysis, 10 ml of sample is pipetted into a beaker and 0.2 ml of ionic strength adjuster (ISA) is added. A typical calibration curve is shown in Figure I.1. Samples with 1000 mg/L Cl or greater are diluted 1:10 with double distilled water and re-analysed.

I.2.3 Nitrate

All samples were analyzed for NO_3 using an Orion model 93-07 nitrate electrode combined with an Orion 90-02 double junction reference electrode attached to the Fischer or Orion Ion Analyzer. The nitrate electrode was calibrated using N standards of 1, 10, 100 ppm N. A typical calibration curve shown in Figure I.2 shows a linear response over most of the range of interest. Samples with NO_3 concentrations beyond the linear range were diluted with double distilled water and re-analysed.

Procedurally, the analysis requires 10 mL of sample to which has been added 0.2 ml of I.S.A. (ionic strength adjuster). The sample is stirred using a magnetic stirrer and a N-nitrate measurement is recorded after the reading stabilizes. Since the instrument is calibrated using nitrogen standards, the nitrate concentration of each sample can be determined by the formula:

$$N \times 4.43 \text{ (mg/L)} = NO_3 \text{ (mg/L)} \qquad (I.3)$$

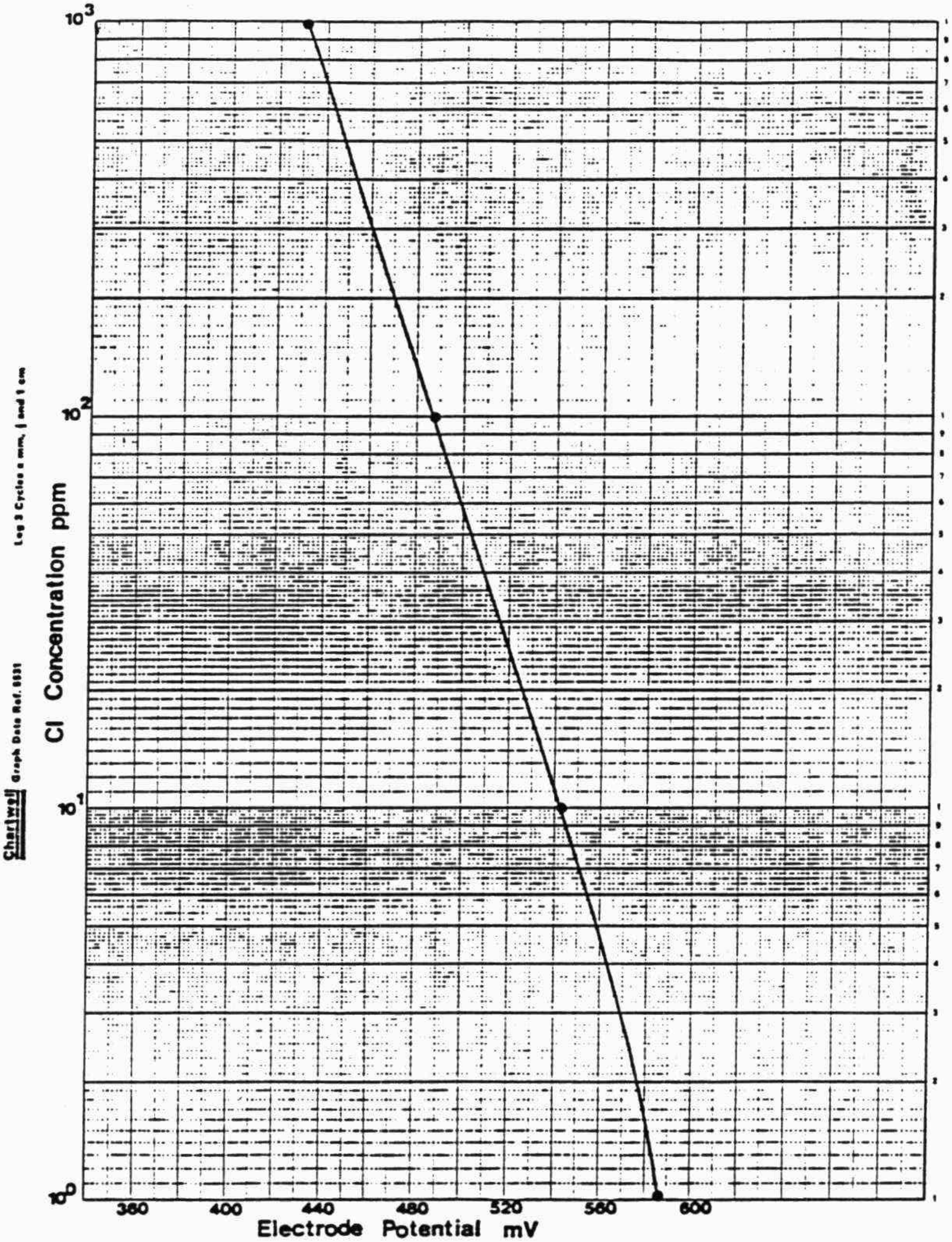


Figure I.1 Calibration curve for chloride

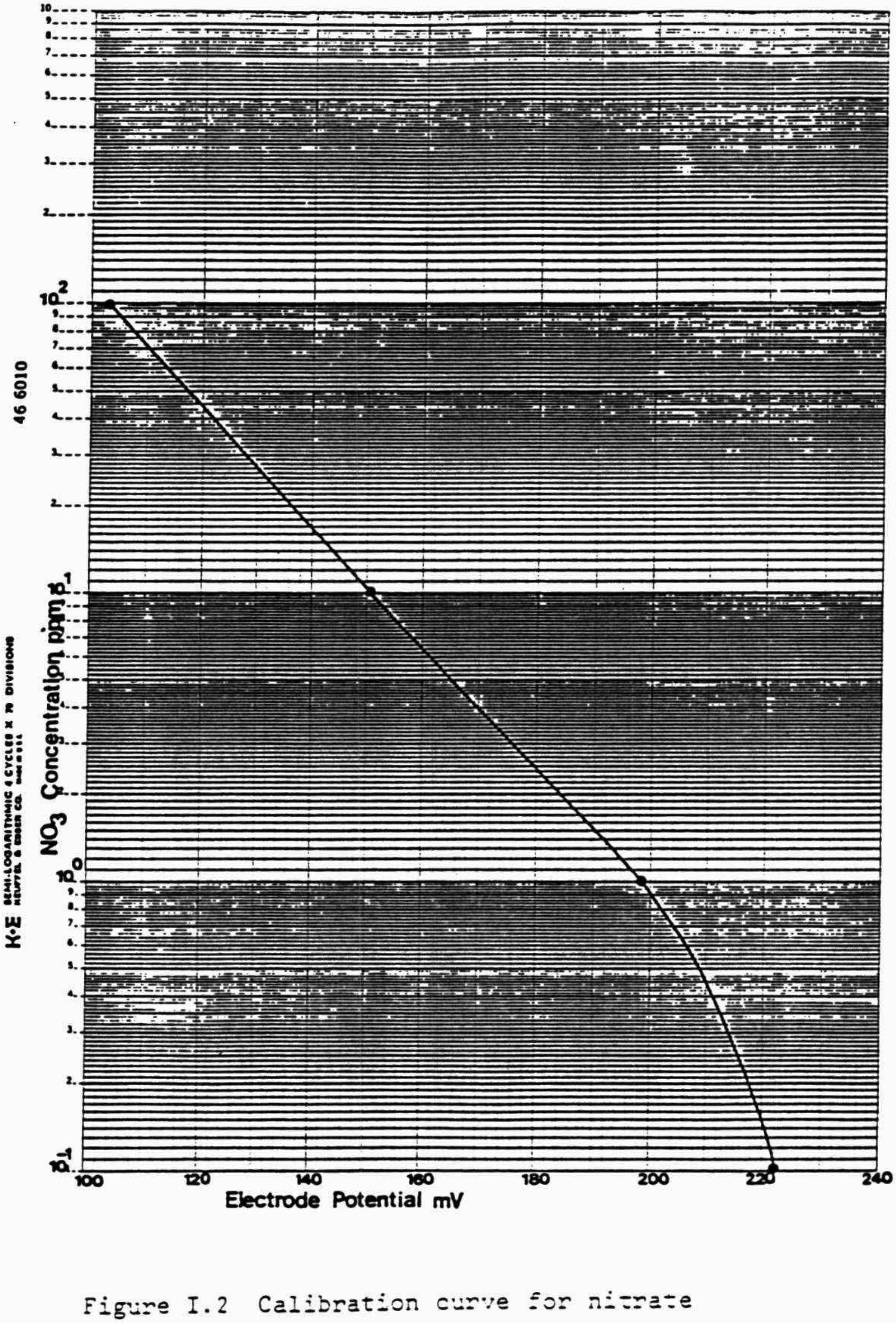


Figure I.2 Calibration curve for nitrate

I.2.4 Fluoride

Fluoride measurements were made using an Orion combination fluoride electrode 96-09 attached to the Fischer or Orion ion analyzer. The fluoride electrode was calibrated using 0.1, 1.0, 10 ppm F standards which were equilibrated to room temperature. A linear response was observed to 1 ppm fluoride as shown in the typical calibration curve in Figure I.3.

In this method, analyses are conducted on 2 mL samples to which has been added 2 mL of total ionic strength adjuster (TISAB) containing cyclohexylene diamine-tetra-acetic acid (CDTA). The CDTA breaks down complexes involving Al^{3+}, Fe^{3+} and the F^- ion (American Public Health Association, 1985). Samples are constantly stirred and measurements are taken after the reading stabilizes. Between measurements the electrode is rinsed in double distilled water and blotted dry.

For very low levels of F^-, a low level measurement technique was used in which low level TISAB without CDTA is added to the sample. The electrode was calibrated using 0.1 and 1.0 ppm F^- standards.

I.3 Colorimetry

Colorimetry is based on absorptiometry, that is, the absorption of electromagnetic radiation by compounds. Commonly the range over which absorbance is determined is approximately 200 to 750 nm. The method is based on the fact that many substances, metals for example, form intensely coloured complexes upon reaction with organic reagents. When radiant energy or light is applied to solutions containing these complexes, certain wavelengths are absorbed as a function of the concentration of the colour forming complex. This in turn can be related to the concentration of the element/ion of interest (Robinson, 1982).

The colorimetric technique was used for the determination of iodide and bromide, using a Cary 14 spectrophotometer and a visible light source.

I.3.1 Iodide

Iodide concentrations of samples were measured using a catalytic reduction method described by Pacey (unpublished). However, the reader is referred to Lloyd et al. (1982) for the relevant reaction,

$$2Ce^{4+} + As^{3+} = 2Ce^{3+} + As^{4+} \qquad (I.4)$$

The reaction involves the reduction of Cerium (Ce^{4+}) by arsenic (As^{3+}) in the presence of iodide which acts as a catalyst. Since Ce^{4+} ions are yellow and cerrous (Ce^{3+}) ions which are colourless, the reaction can be followed photometrically. Details of the method are as follows:

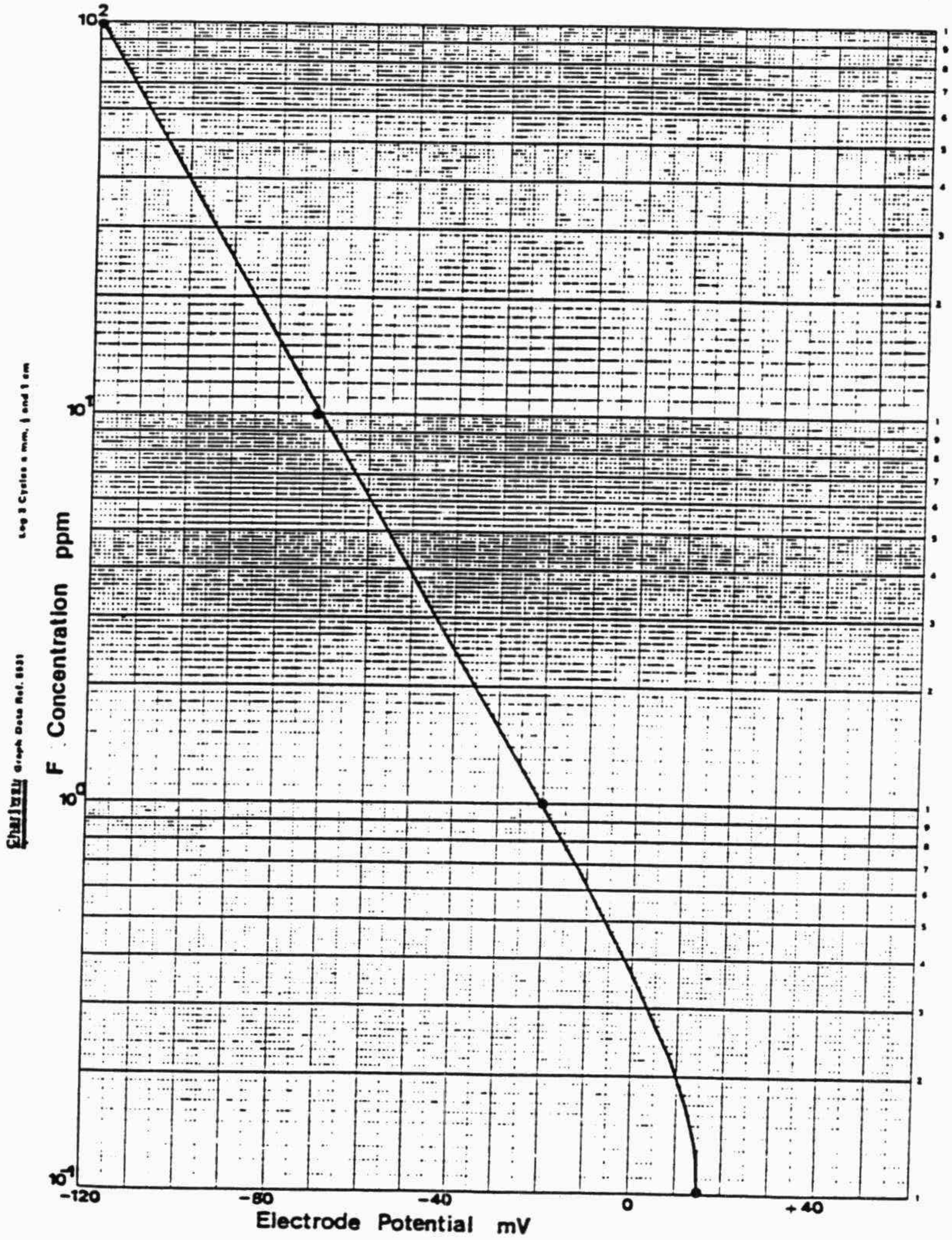


Figure I.3 Calibration curve for fluoride

1) 5 mLs of standard or sample are pipetted into a test tube

2) to each test tube 0.5 mL of 0.1N arsenious acid and 1 drop (0.05 mL) of sodium chloride is added.

3) the mixture is placed in a 30°C water bath

4) 0.5 mL of 0.05 M ceric sulphate is added to each test tube at 4 minute intervals.

5) Exactly 10 minutes after the addition of the ceric sulphate, the colour density of that sample is measured at 420nm on the spectrophotometer.

A typical iodide calibration curve is shown in Figure I.4.

I.3.2 Bromide

Bromide concentrations in all the samples were measured using a phenol red technique. The technique works on the principle that when samples containing bromide ions are treated with a dilute solution of chloramine-T, in the presence of phenol red, , the oxidation of bromide and subsequent bromination of the phenol red occur readily. Unbrominated phenol red is yellow in colour and turns reddish to violet upon formation of the brominated compound. As with iodide, the reaction may be measured photometrically. The method is as follows:

1) 5 mL of standard or sample is pipetted into a test tube

2) to each test tube 0.2 mL of acetate buffer solution and 0.2mL of phenol red solution are added.

3) the mixture is placed in a 30°C water bath

4) 0.05 mL of chloramine-T solution is added to each tube in 4 minute intervals so that exactly 6 minutes after each addition the absorbance can be measured on the spectrophotometer. Measurements were taken at a wavelength of 590nm.

A typical calibration curve is shown in Figure I.5. The calibration curve remains linear up to about 4 mg/L Br.

I.4 Turbidimetry

Turbidimetric methods are similar to colorimetric methods except that they rely upon light absorbance by crystals suspended in solution, rather than upon the absorbance of light by coloured solutions. One problem of the technique is that suspended material in the samples may seriously interfere with the analytical results.

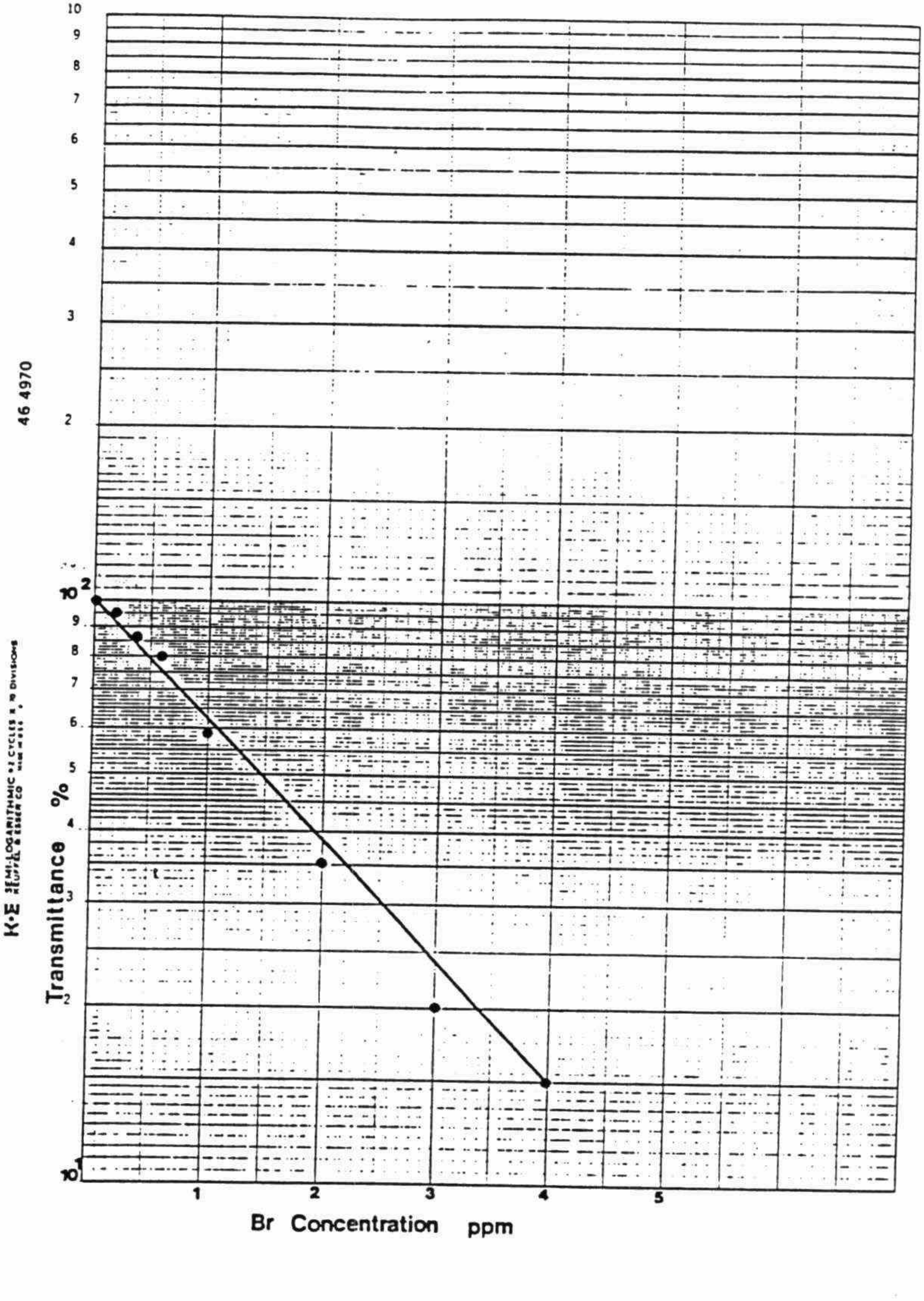


Figure I.5 Calibration curve for bromide

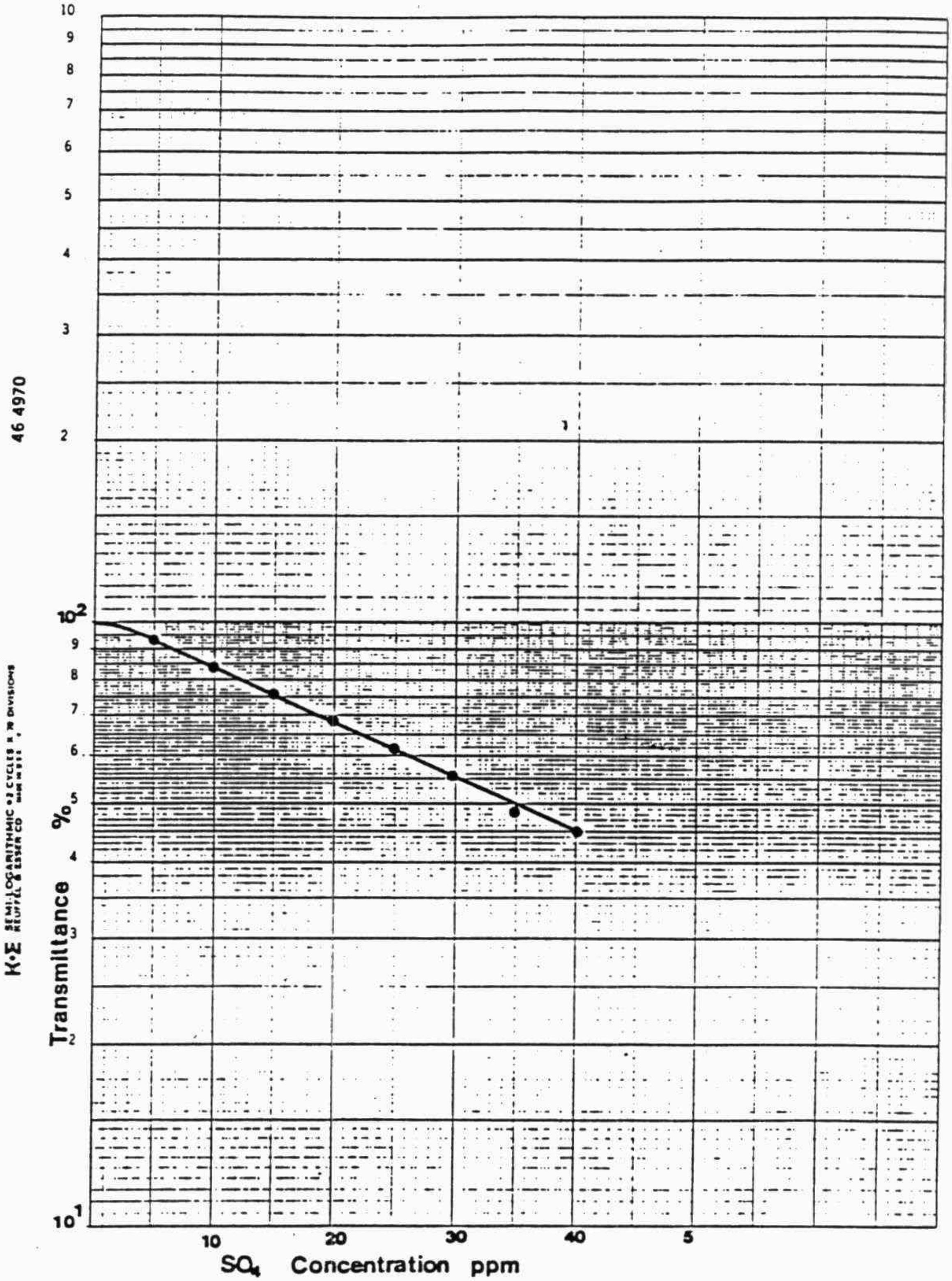


Figure I.6 Calibration curve for sulphate

I.4.1 Sulphate

Sulphate concentration was measured using a turbidimetric method outlined by American Public Health Association (1985). This method is based on the formation of barium sulphate crystals when barium chloride is added to solutions containing sulphate ions in an acetic acid medium. The method is as follows:

1) 50 mL of sample is placed in an Ernlenmeyer flask

2) if the sample is expected to have a sulphate concentration > 15 mg/L, 10 mL of a buffer solution containing sodium acetate, potassium nitrate, and magnesium chloride is added.

3) if the sample is expected to have a sulphate concentration < 15 mg/L, 10 mL of a buffer solution containing sodium acetate, potassium nitrate, magnesium chloride, and sodium sulphate is added.

4) the sample is then stirred with a magnetic stirrer.

5) 0.25 to 0.35g of 20 to 30 mesh $BaCl_2$ is added to the sample, the amount added being such as will dissolve within 10 to 30 seconds. The time of addition is noted to the nearest second.

6) stirring is continued for 1 minute and the absorbance at 420 nm is read after 5 minutes using a Bausch & Lomb Spectronic 20 photometer.

7) a series of standards from 10 to 150 ppm sulphate are used to calibrate the photometer. A typical calibration curve is shown in Figure I.6.

I.5 Atomic Absorption Spectrometry

Atomic absorption spectrometry is based on the principle that valence electrons of atoms absorb quanta of ultraviolet and visible light radiation and undergo a resonance transition from the ground state to a low excited state. The resonance transition is the only important transition in atomic absorption spectrometry (Robinson,1982). If a solution containing a metallic element such as Ca is aspirated into a flame and a beam of monochromatic light of the same wavelength that the Ca atoms would emit, if excited, is passed through the flame, a certain amount of the light will be absorbed and its intensity will decrease. The decrease in intensity of the resonant monochromatic light can be measured using a spectrophotometer. Since the amount of light absorption is directly proportional to the concentration of neutral Ca atoms in the flame, the concentration of the element in the solution may be determined from absorbance measurements.

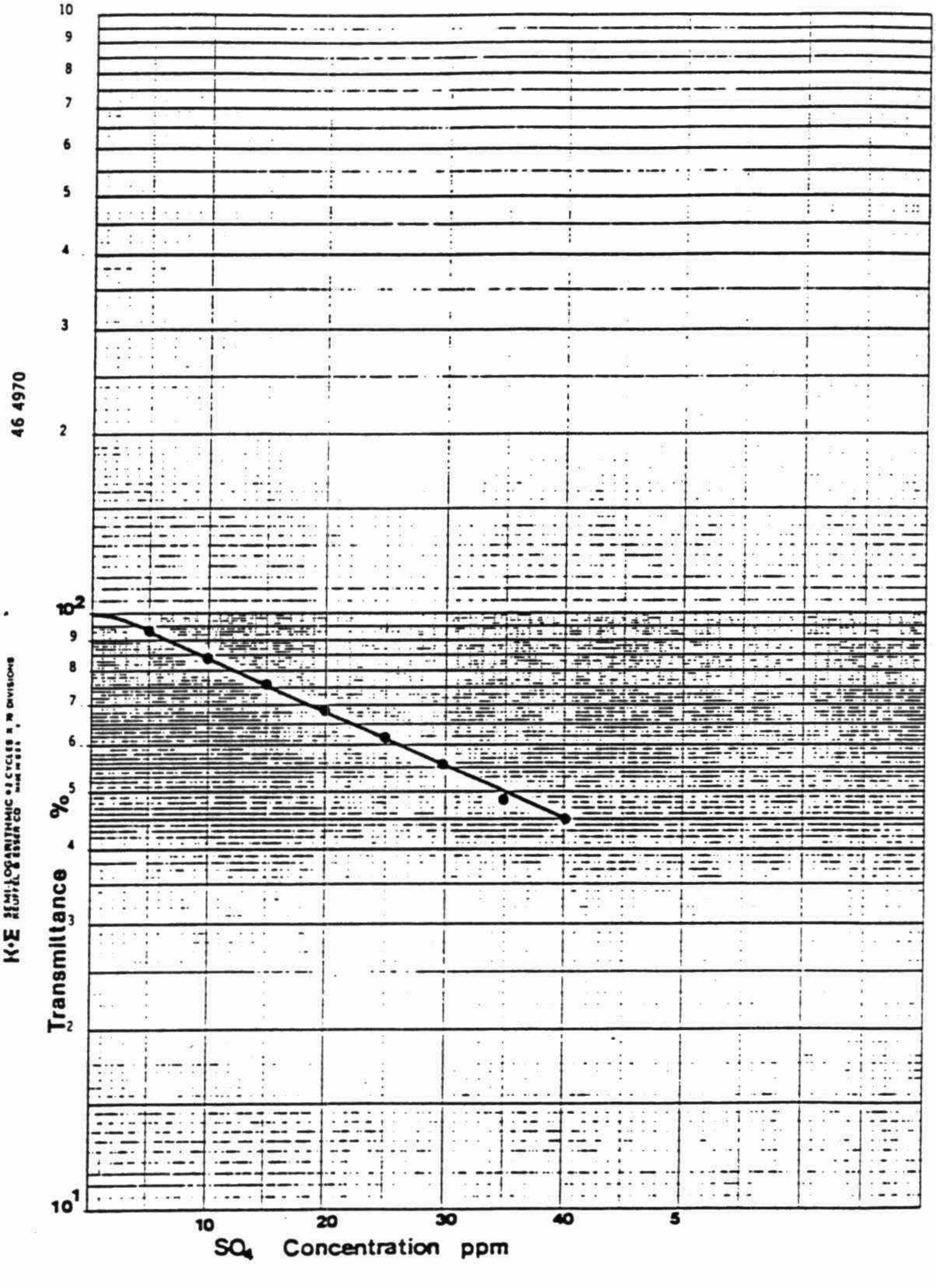


Figure I.6 Calibration curve for sulphate

I.5.1 Calcium and Magnesium

Calcium and magnesium were measured using atomic absorption spectrometry. The atomic absorption unit on the Jarrell Ash model 82-270 was calibrated using Ca and Mg standards of 2, 5, 10, 20, 30, 40, 50, 60, 70 75, and 100 ppm. Percent absorption was recorded, and absorbance was calculated according to the formula:

$$A = 2 - \log (100 - \% \text{ absorption}) \qquad (I.5)$$

To eliminate phosphate interference, 1 mL of lanthanum oxide solution was added to 10 mL of both samples and standards. Calibration curves for magnesium and calcium are shown in Figures I.7 and I.8 respectively. Samples which contained greater than 100 mg/L of Ca or Mg were diluted and rerun.

I.6 Atomic Emission Spectrometry

Atomic emission spectrometry (AES) is based on the principle that atoms which have absorbed radiant energy and have undergone a transition to a high energy state will emit a characteristic amount of energy in returning to the neutral state. In atomic emission spectrography, flame, electrical discharge, plasma, or lasers may be used to excite atoms (Robinson, 1982). Irrespective of the excitation source, the atoms emit photons of light energy as they return to their neutral state. This energy will provide a measure of the number of atoms present.

A.E.S. was used to measure sodium and potassium by means of a Jarrell-Ash flame emission unit. This is described in section I.6.1. A second technique, ICP-AES, in which a plasma (an ionized gas) is inductively coupled to a power source was used to measure 22 trace elements (section I.6.2).

I.6.1 Sodium and potassium

Sodium and potassium were measured using flame emission spectrometry, a technique in which atoms are excited by means of an air-acetylene flame. The Jarrell-Ash spectrophotometer was calibrated using blanks and 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 ppm Na and K standards to which lithium chloride had been added. Percent emission was recorded, and optical density was determined using the formula:

$$\text{optical density} = 2 - \log (\text{percent emission}) \qquad (I.6)$$

The calibration curves for Na and K are shown in Figure I.9 and I.10 respectively.

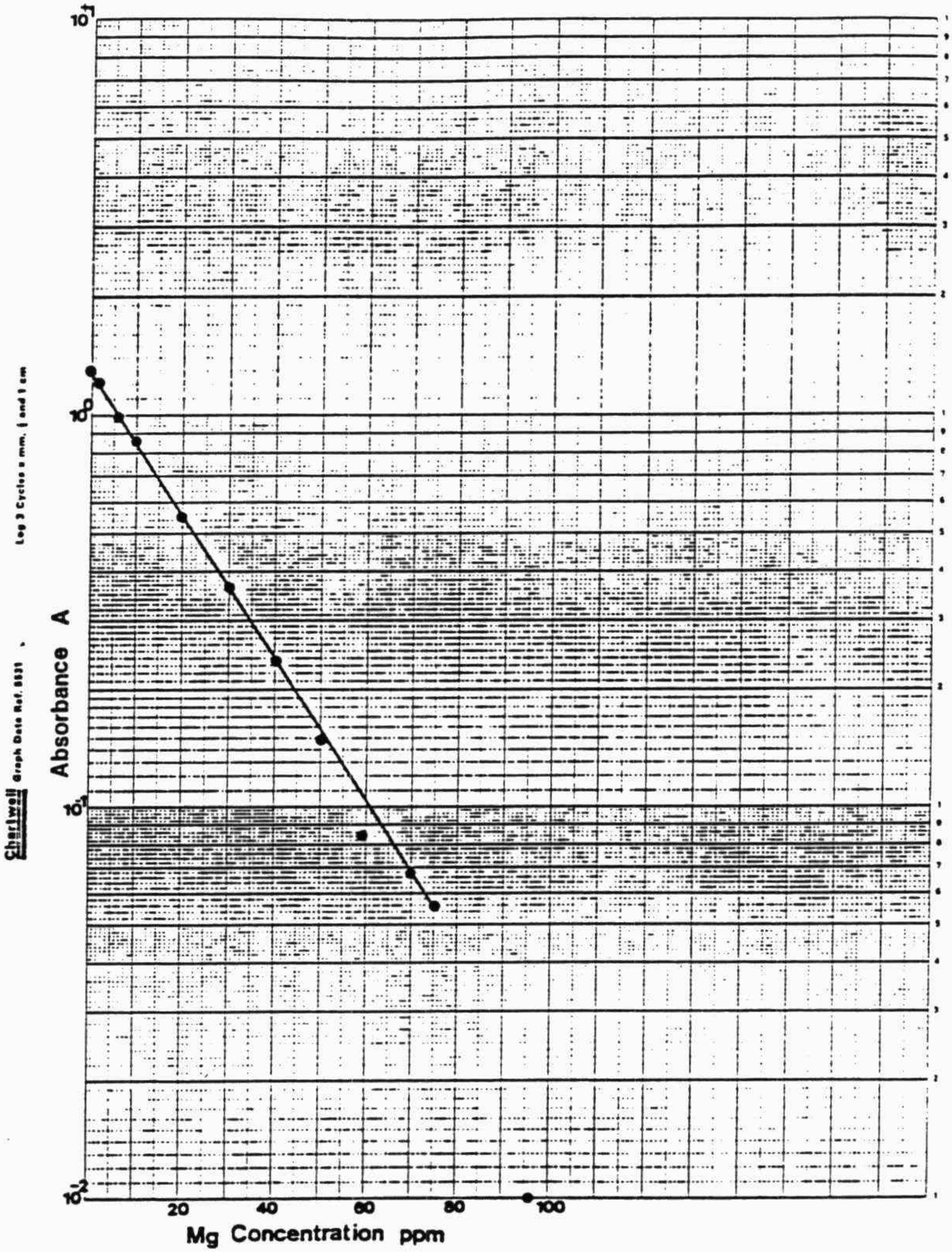


Figure I.7 Calibration curve for magnesium

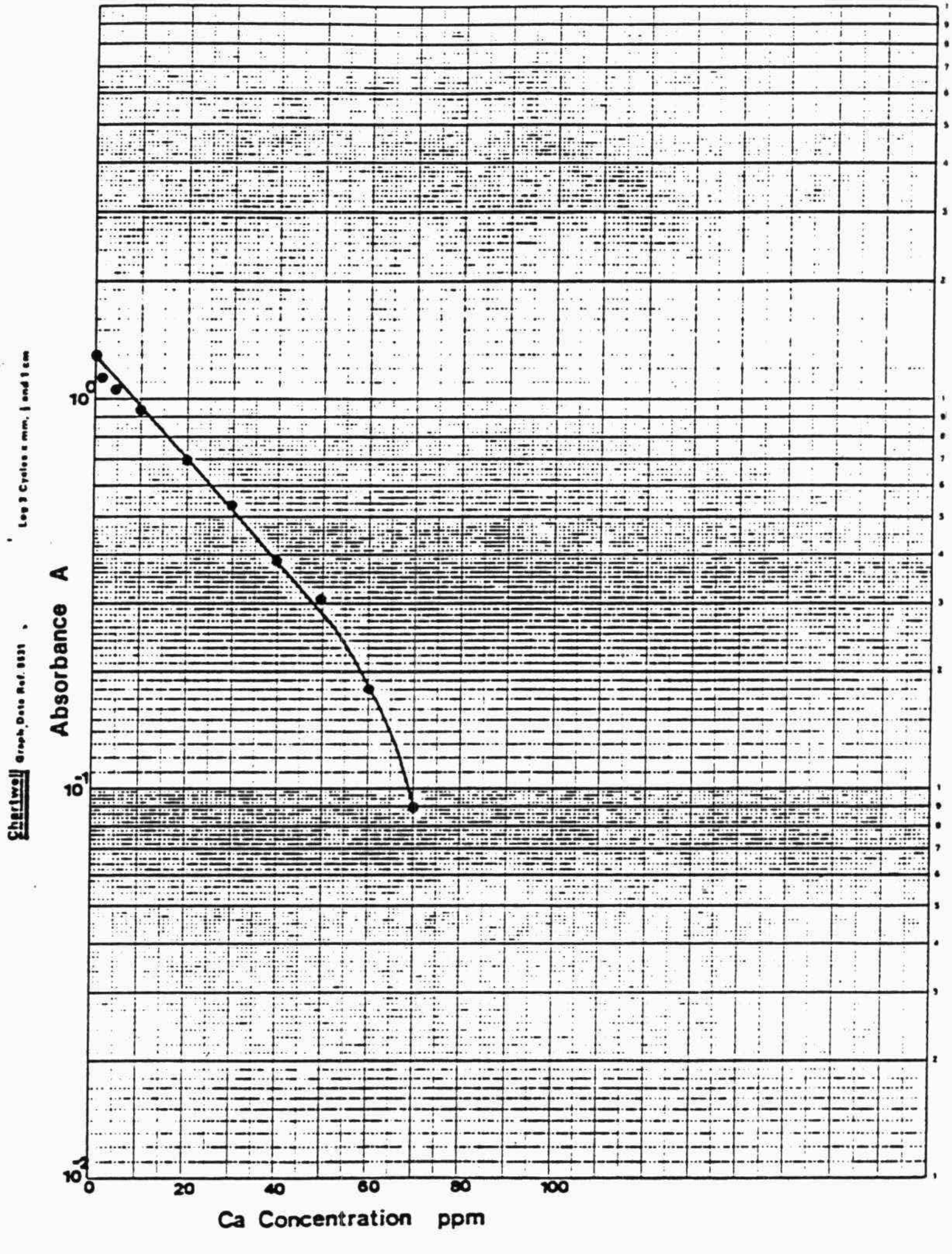


Figure I.8 Calibration curve for calcium

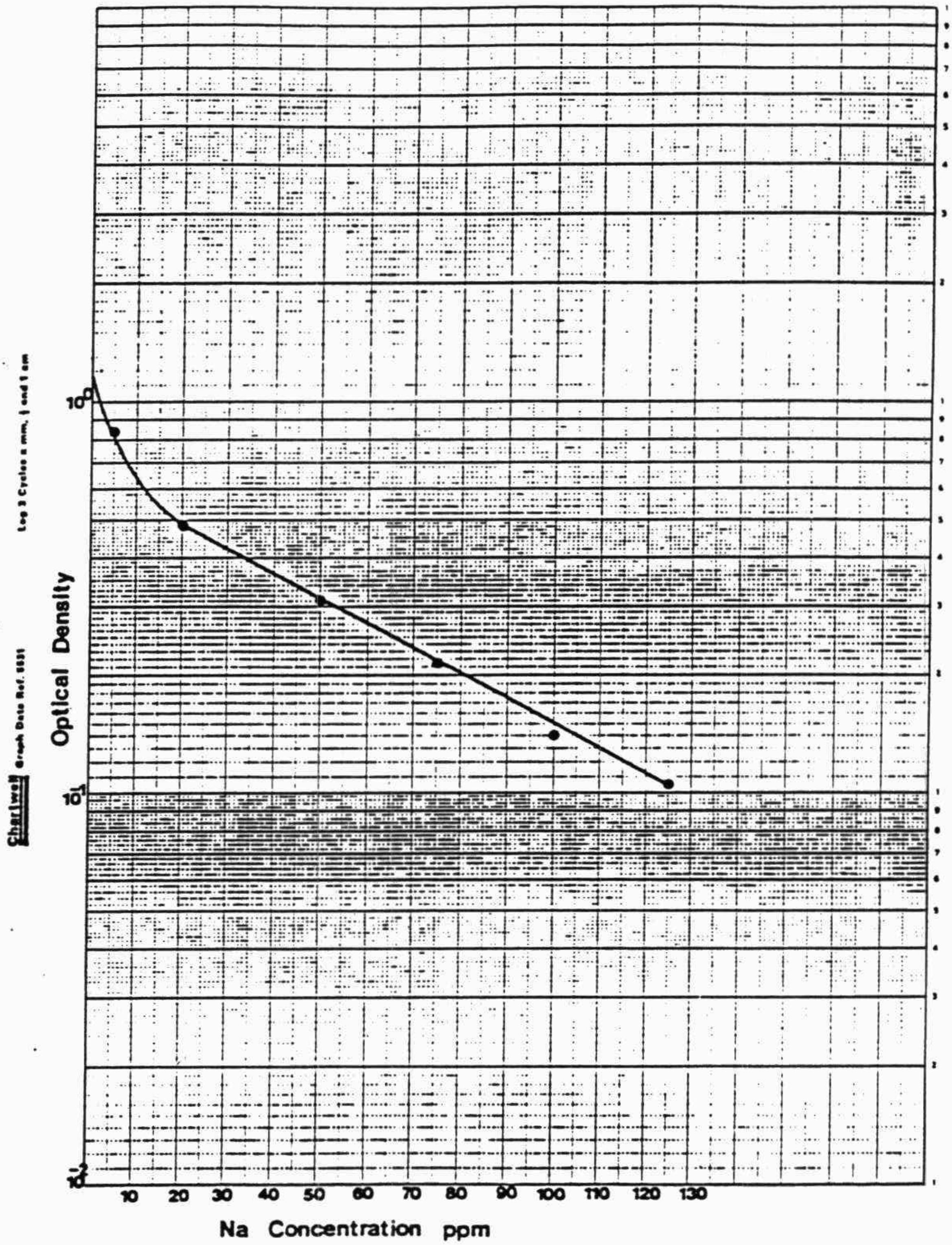


Figure I.9 Calibration curve for sodium

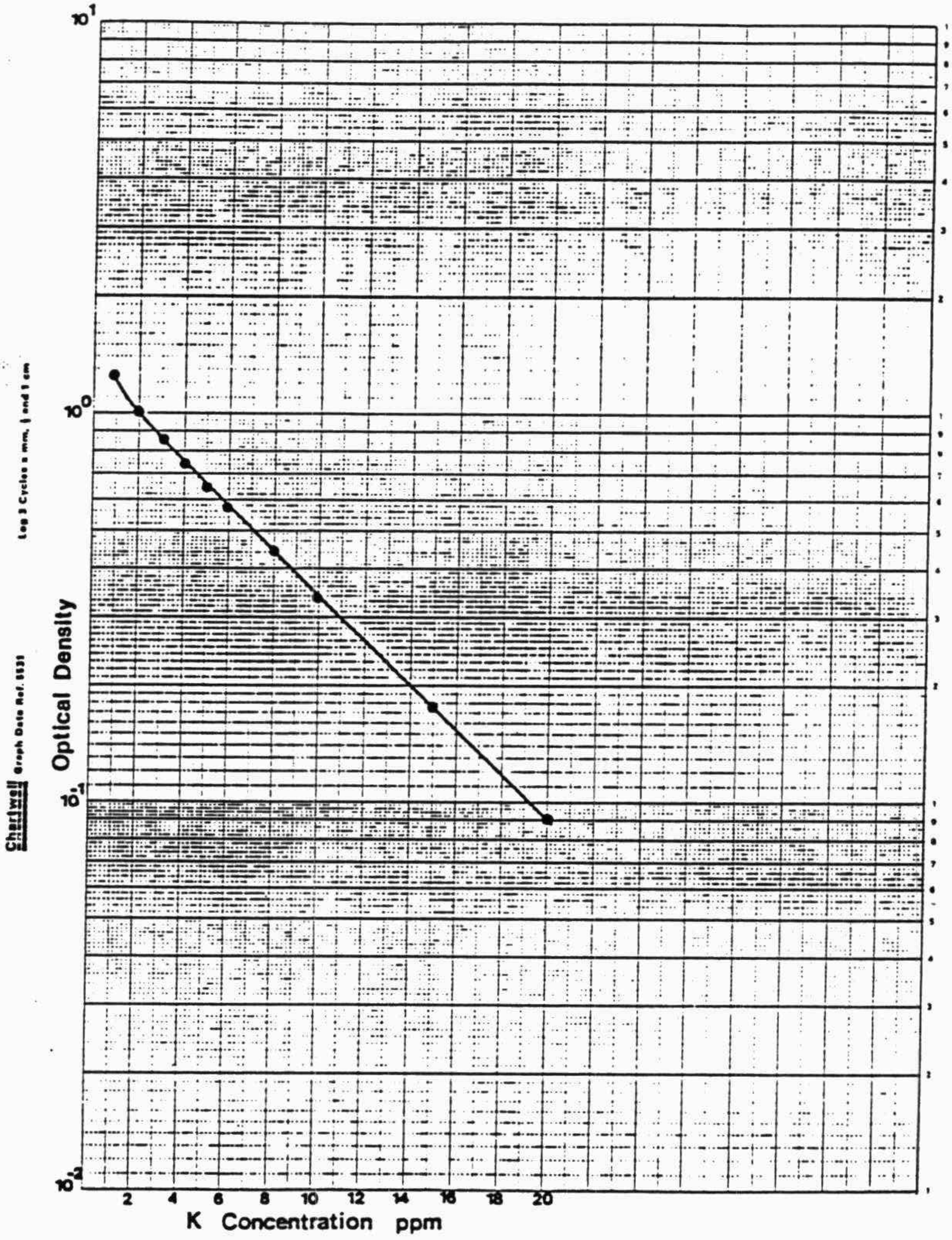


Figure I.10 Calibration curve for potassium

I.6.2 Trace elements

To measure the concentrations of twenty-two elements in the well waters, contaminants, and interstitial pore waters, inductively coupled plasma was used. As mentioned in section I.5, exciting atoms may be accomplished by inductively coupling a plasma (ionized gas) to a power source (Pinta, 1978). The degree of ionization varies. In the inductively coupled plasma system, argon gas is directed into a tube surrounded by an induction coil. An alternating current at a frequency of 30 MHz is applied to the induction coil resulting in the formation of a high frequency magnetic field. This causes the normally non-conductive argon gas to become slightly ionized. The initial few ions are immediately affected by the magnetic field; they begin to oscillate at the same frequency as the RF coil and collide with other argon atoms. This results in the ionization of many argon atoms, and the formation of a plasma. At a temperature of 6500°K and a frequency of 30 MHz the plasma is shaped like a doughnut (Pinta, 1978; Robinson, 1982). A second stream of argon is directed around the central argon stream (the plasma) to prevent contact and the potential melting of the quartz tubing.

Once the plasma is formed, the sample is aspirated into the interior of the plasma via a nebulizer. Most of the sample is atomized by the heat of the plasma (the sample atoms collide with argon ions and become ionised (Pinta, 1978)). This excitation results in intense emission and a spectrometer is used to isolate the emission spectral lines (Robinson, 1982). Technically, this is achieved by directing the emitted radiation through a primary slit and onto a grating which breaks it into component wavelengths. The radiation then passes through exit slits mounted on the focal plane, and onto a photomultiplier. In the case of the ICP unit at the University of Toronto, there are thirty-one exit slits to allow for the monitoring of thirty-one emission lines simultaneously. In the case of this instrument, each emission line represents a different element.

A total of 22 elements were analyzed using ICP-AES and these are shown in Table I.2 along with their theoretical detection limit (T.D.L.) and determination limit (D.L. = five times the theoretical detection limit).

The well water samples were prepared for ICP analysis by preconcentration. For this procedure, 100 ml of filtered, acidified, well water is boiled almost to dryness in a pyrex beaker. One half ml of ultrapure nitric acid and 1 ml of double distilled water are added to the beaker and the sample is once again evaporated to near dryness. In the final step, 0.5 ml of Ultrapure nitric acid and 1 ml of double distilled water are added to the beaker and the sample is evaporated for approximately 5 minutes. Sample volume is then adjusted to 10 ml with double distilled water in a 10 ml Erlenmeyer flask. Interstitial water samples and contaminants were not preconcentrated due primarily to inadequate initial volume size.

Table I.2 Parameters determined by ICP-AES analysis

Element	T.D.L(mg/L)	D.L.(mg/L)
Be	0.00029	0.001
Ba	0.00025	0.001
Fe	0.0012	0.006
Cr	0.0024	0.012
S	0.0132	0.066
Mg	0.0137	0.0685
As	0.0226	0.113
V	0.0016	0.008
Se	0.0823	0.2115
Mo	0.0068	0.034
Al	0.0164	0.082
Ca	0.0014	0.007
Zn	0.004	0.02
Cu	0.0023	0.0115
Sb	0.0377	0.1885
Pb	0.0460	0.23
Cd	0.0032	0.016
Co	0.0034	0.017
Ni	0.0137	0.0685
P	0.0357	0.1785
B	0.0045	0.0225
Mn	0.0006	0.0030

I.7 Volumetric methods

Volumetric methods involve the titration of reagents to a specific chemical endpoint. The methods were used to measure chloride, carbonate and bicarbonate concentrations.

I.7.1 Carbonate

Carbonate concentration was determined using the following procedure,

1) 50 mL of water sample is pipetted into an Erlenmeyer flask

2) 10 drops of phenolphthalein indicator are added using a Pasteur pipet

3) if the sample does not turn pink, there is no carbonate present

4) if the sample does turn pink, carbonate is present and the sample is then titrated with 0.05 N H_2SO_4 until the sample becomes colourless

6) the litre volume (mL) is recorded and the concentration of CO_3 in epm is determined by the formula:

$$CO_3 \text{ (epm)} = \text{litre volume (mL)} \times 2 \qquad (I.7)$$

I.7.2 Bicarbonate

Bicarbonate analysis was performed using the following method,

1) following the CO_3 titration, 6 drops of bromcresol green indicator are added to the sample using a Pasteur pipet

2) the sample is titrated using 0.05 N H_2SO_4 until the solution turns green

3) the total buret reading (mL) is recorded and the bicarbonate concentration is determined as follows:

if CO_3 was absent the buret reading in mL = epm HCO_3

if CO_3 was present,

$$\text{total litre mL} - ((CO_3 \text{ litre mL}) \times 2) = \text{epm } HCO_3 \qquad (I.8)$$

I.7.3 Chloride

In addition to using a specific ion electrode, chloride was also measured using the argentometric method as described in Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1985). The method works on the principle that potassium chromate can be used to determine the end point of silver nitrate titrations.

The concentration of chloride is calculated according to the formula:

$$\text{mg/L Cl} = \text{(mL titration for sample} - \text{mL titration for blank)} \times (\text{normality of } AgNO_3 \times 35450) / \text{mL sample used} \qquad (I.9)$$

I.8 Instrumental Neutron Activation Analysis

In neutron activation analysis, the sample is exposed to a source of thermal neutrons. When these neutrons pass close to a target nucleus, the action of nuclear forces can cause the neutron to penetrate into the nucleus, forming a new nucleus which is (usually) radioactive or excited (Robinson, 1982). The new nucleus has the same atomic number (Z) but a different (one unit higher) mass number (A) reflecting its increased nucleus mass.

Subsequently, the new radioactive nucleus decays to either a stable or radioactive nucleus by emitting radiation. The radiation emitted may be in a number of forms, but in INAA only the gamma rays are measured, generally in the energy range 30KeV to 1MeV. The intensity of this radiation is a function of the mass of material present (Guinn, 1981).

As a source of thermal neutrons, the University of Toronto INAA laboratory uses a Slowpoke II nuclear reactor. This model provides a thermal neutron flux of 5×10^{11} n/cm²s (Guinn, 1981).

The neutron activation technique is applicable to the measurement of a wide range of elements. However, the measurement technique will depend on the rates of decay of the isotopes formed by the neutron bombardment. For example some elements form short-lived isotopes which must be measured almost immediately; others form long-lived isotopes which can be counted after an extended period of time.

I.8.1 Short-lived isotope neutron activation analysis.

Neutron activation analysis was carried out 20 samples to measure the concentration of short-lived isotopes of the following elements: Na, Cl, Ba, Ti, Mg, Ca, Mn, V, and Al. Exactly 1.0 g of sediment was weighed into small polyethylene vials supplied by the Nuclear reactor lab. Sediment samples were irradiated for 2 minutes at a flux of 2 kW and counted 18 minutes later for a period of 300 s (5 minutes). The activity of each element was calculated using the formula,

$$\text{Activity (A)} = \text{peak count (p)} - \text{background count (b)} \quad (\text{I.10})$$

I.8.2 Long-lived Isotope Neutron Activation Analysis

Neutron activation analysis was conducted on 6 sediment samples to measure the concentration of the long-lived isotopes of the following elements, La, Sc, Co, Cr, Na,and Fe. Exactly 0.3 g of sediment was weighed into polyethylene vials which were cut to size and subsequently sealed using a soldering iron. The sediments were irradiated for 16 hours at a flux of 5 kW. Samples were counted after 7 days for 600s (10 min) to measure medium lived isotopes La, Fe, and Na. A second count was performed after 14 days for 6000s (100 mins) to measure the long-lived isotopes of Sc, Cr, Fe, and Co. The activity of the sample was determined as outlined for short-lived isotopes.

After neutron activation analysis for short lived and long lived isotopes was completed, standards were made for elements for which the measurement error was less than 30%. For short lived isotopes INNA standards were made for Na, Ca, Mg, Ti, Ba, Cl, V, Mn. Table I.3 shows the amount and type of chemical used for each standard. For long lived isotope INNA, the University of Toronto in house standard UTB-1 was used. Table I.4 shows the composition of the standard based on studies conducted by Barnes and Gorton (1985).

Table I.3 Neutron activation standards

Element	Chemical	Weight of Chemical (mg/L)
Ba	BaCO3	100 - 200 mg
Ti	TiO2	100 - 300 mg
Mg	Mg metal	20 - 100 mg
Na	NaCl (dry)	100 mg
Cl	NaCl (dry)	100 mg
Al	Al foil	100 mg
Ca	$CaCO_3$	200 - 400 mg
Mn	Mn AA Standard (1000ppm)	0.5 ml or 0.5 mg
V	V_2O_5 (1000ppm solution)	0.5 ml or 0.5 mg

Table I.4 Neutron activation standard UTB-1*

Element	Concentration in Standard UTB-1 (mg/L)
Barium	590
Cobalt	49
Chromium	35
Iron (Fe_2O_3)	15.05
Lanthanum	27
Sodium (Na_2O)	2.73
Rubidium	28

* after Barnes and Gorton (1984)

Groundwater Samples Duffins Creek-Rouge River Basins Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I++	Br	CO3
83-117	1A	7.70	5.76	4.96	0.62	0.00	0.12	0.00
83-32	1A	7.30	10.72	2.95	0.05	0.00	0.40	0.00
83-79	1A	7.00	0.95	5.00	0.07	2.00	0.04	0.00

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
83-117	262.30	53.94	14.02	4.50	1.00	17.73	0.30
83-32	225.70	63.58	18.04	5.00	0.50	18.93	0.32
83-79	323.30	72.96	23.37	5.20	1.50	93.10	0.49

+ not determined

++ ug/L

Groundwater Samples   Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination Limit		0.0003	0.0178	0.0034	0.0082	0.0020	0.0068	0.0006
83-117	1A	0.0131	*	*	*	0.0193	*	0.7412
83-32	1A	0.0241	*	*	*	0.0094	*	0.3500
83-79	1A	0.1070	0.0323	*	0.1461	0.5103	*	0.3597

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As	Se
	0.0230	0.0012	0.0017	0.0012	0.0016	0.0066	0.0113	0.0212
83-117	*	0.0083	*	0.0043	*	5.9093	*	*
83-32	*	0.0249	*	0.0002	*	6.3094	*	*
83-79	*	0.0382	*	*	*	31.0328	*	*

SAMPLE	Sb	V	B	Ba	Be
	0.0186	0.0008	0.0023	0.0001	0.0001
83-117	*	0.0025	*	0.1361	0.0008
83-32	*	0.0008	*	0.1283	*
83-79	*	0.0011	*	0.0258	*

* below ICP determination limit

Groundwater Samples   Duffins Creek-Rouge River Basins   Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I**	Br	CO3
82-7	1U	7.40	13.51	17.99	0.08	0.00	0.25	0.00
82-12	1U	7.30	16.03	20.32	0.10	1.00	0.34	0.00
82-19	1U	6.90	22.20	15.95	0.12	+	0.76	0.00
82-20	1U	7.20	9.70	10.08	0.15	17.20	0.13	0.00
82-23	1U	7.50	5.70	20.64	0.13	11.00	+	0.00
82-24	1U	7.40	5.76	11.00	0.05	0.00	0.00	0.00
82-44	1U	7.50	6.07	10.42	0.13	0.00	0.28	0.00
83-19	1U	7.00	0.42	7.71	0.10	5.00	0.40	0.00
83-46	1U	7.50	5.98	26.06	0.05	0.00	0.13	0.00
83-49	1U	7.50	12.20	10.64	0.60	0.00	0.12	0.00
83-56	1U	7.40	13.30	10.08	0.69	2.20	0.08	0.00
83-58	1U	7.40	104.11	67.74	0.05	0.00	0.28	0.00
83-88	1U	7.65	4.30	15.68	0.13	1.00	0.10	0.00
83-105	1U	7.20	10.40	26.05	0.11	0.00	0.00	0.00
83-112	1U	7.55	5.98	31.27	0.14	0.00	0.21	0.00
83-115	1U	7.60	5.54	26.06	0.12	0.00	+	0.00
83-116	1U	7.55	5.32	20.84	0.11	0.00	0.00	0.00
83-125	1U	+	+	10.42	0.10	0.00	0.73	0.00
83-126	1U	7.60	+	10.42	0.08	0.00	+	0.00
83-199	1U	7.60	5.85	15.63	0.13	3.00	+	0.00
83-205	1U	7.45	7.17	26.05	0.09	5.90	0.36	0.00
83-211	1U	6.90	11.06	13.16	0.07	1.00	0.00	0.00
83-139	1U	7.50	+	31.26	0.09	2.20	+	0.00
83-47	1U	7.35	12.60	31.91	0.58	0.00	0.00	0.00
83-124	1U	7.45	+	15.63	0.08	0.00	0.92	0.00
82-28	1U	7.45	5.70	15.63	0.13	0.00	+	0.00
83-210	1U	7.70	5.32	15.63	0.14	0.00	0.08	0.00
83-186	1U	7.35	12.85	+	1.32	+	0.28	0.00
83-113	1U	7.25	20.35	41.69	0.15	0.00	0.70	0.00
83-163	1U	7.50	6.50	144.95	0.06	23.00	0.40	0.00
83-104	1U	7.30	101.89	89.83	0.06	0.00	0.30	0.00
83-122	1U	7.35	43.41	140.70	0.12	0.00	0.36	0.00
83-133	1U	7.40	4.83	110.38	+	14.50	0.60	0.00
83-90	1U	7.30	7.26	99.81	0.14	0.00	0.71	0.00
83-80	1U	6.90	5.63	+	0.08	10.00	0.84	0.00
83-100	1U	7.40	33.67	24.82	0.17	0.00	0.26	0.00
83-40	1U	7.50	5.32	23.49	0.08	0.00	0.30	0.00
83-59	1U	7.50	9.52	37.99	0.07	7.80	0.10	0.00
83-83	1U	7.45	31.24	26.06	0.15	17.20	0.10	0.00
83-94	1U	7.25	34.60	40.92	0.08	0.00	0.00	0.00
82-42	1U	+	+	+	+	+	+	+
83-110	1U	7.00	+	+	+	+	+	+
83-121	1U	+	+	+	+	+	+	+

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
82-7	274.50	77.48	22.49	7.50	2.00	35.77	0.45
82-12	323.30	87.47	21.12	14.00	2.50	85.94	0.47
82-19	231.80	68.01	22.68	4.80	2.00	34.66	0.38
82-20	274.50	43.02	22.07	9.50	2.00	9.95	0.33
82-23	280.60	67.11	15.79	6.50	0.50	25.49	0.33
82-24	298.90	67.05	16.09	4.50	2.50	30.56	0.36
82-44	311.10	80.87	16.64	2.50	1.50	51.00	0.29
83-19	274.50	47.99	16.86	6.00	1.50	10.15	0.29
83-46	292.80	70.05	16.64	4.00	5.00	46.81	0.30
83-49	286.70	84.77	3.19	3.00	5.00	16.57	0.32
83-56	311.10	84.32	16.42	2.50	1.00	39.00	0.41
83-58	341.60	146.38	18.71	19.00	1.80	40.83	0.71
83-88	250.00	53.00	15.85	3.50	4.50	18.19	0.21
83-105	370.20	110.16	17.08	7.00	5.00	64.79	0.59
83-112	256.20	76.00	13.07	6.00	1.50	27.11	0.28
83-115	268.40	65.81	15.15	2.50	2.50	8.94	0.28
83-116	268.40	66.91	13.74	2.00	0.00	7.60	0.29
83-125	305.00	77.70	19.68	2.00	0.00	31.72	0.35
83-126	317.20	98.44	18.56	2.50	0.00	44.63	0.38
83-199	341.60	85.80	18.21	6.00	2.50	49.99	0.39
83-205	335.50	100.68	23.89	9.00	1.00	62.58	0.47
83-211	298.90	62.32	20.15	8.00	1.50	17.22	0.38
83-139	347.70	67.50	36.61	13.50	3.00	64.91	0.50
83-47	298.90	112.16	8.76	+	+	20.75	+
83-124	353.80	102.42	12.80	1.80	0.00	23.12	0.39
82-28	298.60	67.77	24.77	5.70	2.50	55.07	0.39
83-210	326.35	55.71	19.57	11.00	2.30	1.65	+
83-186	439.20	124.93	19.46	+	+	70.42	0.51
83-113	262.30	98.46	15.73	7.00	1.80	31.30	0.48
83-163	238.10	73.36	35.28	61.50	46.50	120.61	1.38
83-104	353.80	130.07	14.73	40.50	3.00	46.54	0.73
83-122	323.30	125.73	18.41	34.50	2.00	40.12	0.67
83-133	256.20	43.00	51.00	46.50	2.10	35.20	0.67
83-90	311.10	105.94	27.73	24.00	3.00	96.89	0.62
83-80	359.90	73.10	41.26	15.20	1.00	158.40	0.78
83-100	399.55	109.84	12.97	26.00	1.00	39.74	0.46
83-40	341.60	86.63	12.26	16.50	0.80	30.78	0.40
83-59	384.30	91.37	20.84	20.00	3.00	79.26	0.56
83-83	314.20	69.55	47.52	34.50	17.00	120.61	+
83-94	408.70	111.45	24.95	33.50	3.30	100.64	0.67
82-42	+	40.38	7.69	9.50	0.00	20.20	0.28
83-110	+	50.30	16.72	+	+	9.59	0.28
83-121	+	55.89	11.94	+	+	17.97	0.25

+ not determined

++ ug/L

Groundwater Samples Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination Limit		0.0003	0.0178	0.0034	0.0002	0.0020	0.0068	0.0006
83-104	1U	0.0019	0.0272	*	0.0200	0.0538	0.0080	0.0560
83-105	1U	0.0017	0.0200	*	0.0275	0.0196	0.0070	0.0343
83-110	1U	0.0181	0.0192	*	0.0031	0.0072	*	1.3355
83-112	1U	0.0143	*	*	0.0011	0.0027	*	0.1487
83-113	1U	0.0016	*	*	0.0194	1.1089	*	0.0223
83-115	1U	0.0142	*	*	0.0009	0.2253	*	*
83-116	1U	0.0233	*	*	0.0009	0.0135	*	0.1252
83-121	1U	0.0586	0.0192	*	0.0937	0.2276	*	0.7997
83-124	1U	0.0015	*	*	0.0032	0.2256	*	*
83-125	1U	0.0362	*	*	*	0.0948	*	0.6996

SAMPLE	Pb 0.0230	Cu 0.0012	Co 0.0017	Cr 0.0012	Cd 0.0016	S 0.0066	As 0.0113	Se 0.0212
83-104	*	0.0266	*	0.0030	*	15.5148	0.0114	*
83-105	*	0.0734	*	0.0025	*	21.5968	0.0115	*
83-110	*	0.0073	*	0.0031	*	3.1957	*	*
83-112	*	0.0129	*	*	*	9.0382	*	*
83-113	*	0.0343	*	*	*	10.4328	*	*
83-115	*	0.0263	*	*	*	2.9797	*	*
83-116	*	0.0101	*	*	*	2.5325	*	*
83-121	*	0.0227	*	0.0032	*	5.9905	*	*
83-124	*	0.0213	*	0.0001	*	7.7079	*	*
83-125	*	0.0118	*	*	*	10.5738	*	*

SAMPLE	Sb 0.0186	V 0.0008	B 0.0023	Ba 0.0001	Be 0.0001
83-104	*	0.0022	0.0041	0.0542	*
83-105	*	0.0028	*	0.0512	0.0001
83-110	*	0.0028	0.0009	0.2094	0.0014
83-112	*	0.0022	0.0444	0.1596	*
83-113	*	*	0.0555	0.0504	*
83-115	*	0.0022	*	0.1154	*
83-116	*	0.0025	*	0.1096	*
83-121	*	0.0038	0.0154	0.1257	0.0009
83-124	0.0219	0.0029	*	0.0495	*
83-125	*	0.0026	*	0.0448	0.0002

Groundwater Samples Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination Limit		0.0003	0.0178	0.0034	0.0082	0.0020	0.0068	0.0006
83-122	1U	0.0008			0.0111	0.0419		0.0076
83-126	1U	0.0140	*	*	0.0017	0.0220	*	0.0715
83-133	1U	0.0230	0.0224	*	0.0436	0.0055	*	0.1640
83-139	1U	0.0055	*	*	0.0003	0.0187	*	*
83-163	1U	0.1667	0.0415	*	0.1030	0.0072	0.0073	0.0117
83-186	1U	0.0089	*	*	0.0358	0.0192	0.0074	0.0300
83-19	1U	0.0459	0.0195	*	0.0048	0.2041	*	4.3719
83-199	1U	0.0762	0.0324	*	*	0.0451	*	2.4043
83-205	1U	0.0488	*	*	0.0032	0.6053	*	0.0737
83-210	1U	0.1362	*	*	*	0.4509	*	3.0652
83-211	1U	0.0153	0.0210	*	0.0305	0.1240	*	0.0761

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As	Se
	0.0230	0.0012	0.0017	0.0012	0.0016	0.0066	0.0113	0.0212
83-122	*	0.0286	*	0.0008	*	16.0388	*	*
83-126	*	0.0175	*	0.0001	*	14.0778	*	*
83-133	*	0.0447	*	*	*	13.9530	*	*
83-139	*	0.0139	*	0.0009	*	21.6368	*	*
83-163	*	0.0917	*	0.0007	*	40.2018	0.0226	*
83-186	*	0.0314	*	0.0025	*	23.4718	0.0125	*
83-19	*	0.0184	*	0.0030	*	3.3844	*	*
83-199	*	0.0194	*	*	*	16.6628	*	*
83-205	*	0.0174	*	0.0005	*	20.8588	*	*
83-210	*	0.0164	*	*	*	0.5485	*	*
83-211	*	0.1065	*	0.0019	*	5.7407	*	*

SAMPLE	Sb	V	B	Ba	Be
	0.0186	0.0008	0.0023	0.0001	0.0001
83-122	0.0311	0.0037	0.0004	0.1037	*
83-126	0.0229	0.0030	0.0034	0.0965	*
83-133	*	0.0021	0.0608	0.1131	*
83-139	*	0.0035	0.0140	0.1279	*
83-163	0.0555	0.0033	0.0445	0.1880	*
83-186	0.0196	0.0035	0.0024	0.2920	0.0001
83-19	*	0.0025	0.0106	0.1006	*
83-199	*	0.0011	0.0352	0.0058	0.0006
83-205	0.0241	0.0033	0.0016	0.1106	*
83-210	*	0.0009	0.0328	0.3696	0.0007
83-211	0.0163	0.0018	0.0226	0.2162	*

* below ICP determination limit

Groundwater Samples Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE Determination Limit	Type	Mn 0.0003	P 0.0178	Mo 0.0034	Al 0.0082	Zn 0.0020	Ni 0.0068	Fe 0.0006
82-12	1U	0.0023	0.4859	+	0.0315	0.0140	0.0101	0.0564
82-19	1U	0.0241	+	+	+	0.0750	+	0.0007
82-20	1U	0.0241	+	+	+	0.0750	+	0.0007
82-23	1U	0.0165	+	+	0.0081	0.0635	+	0.0624
82-24	1U	0.0229	0.0219	+	0.0062	0.0071	+	1.1501
82-28	1U	0.2404	+	+	+	0.0127	0.0077	0.1283
82-42	1U	0.0021	+	+	0.1189	0.0298	+	0.1622
82-44	1U	0.0014	0.0188	+	+	0.1298	0.0113	0.0493
82-7	1U	0.0026	0.0186	+	+	0.0229	0.0092	0.0465
83-100	1U	0.0010	+	+	0.0079	0.1910	+	0.0685

SAMPLE	Pb 0.0230	Cu 0.0012	Co 0.0017	Cr 0.0012	Cd 0.0016	S 0.0066	As 0.0113	Se 0.0212
82-12	+	0.0295	+	0.0026	+	20.6478	0.0133	+
82-19	+	0.0297	+	0.0028	+	11.5518	+	+
82-20	+	0.0144	+	0.0021	+	3.3182	+	+
82-23	+	0.0215	+	+	+	0.4959	+	+
82-24	+	0.0181	+	0.0032	+	12.8548	+	+
82-28	+	0.0305	+	+	+	10.3558	+	+
82-42	+	0.0488	+	0.0011	+	9.4013	+	+
82-44	+	0.0123	+	+	+	16.9988	+	+
82-7	+	0.0290	+	0.0026	+	11.9220	+	+
83-100	+	0.0256	+	0.0029	+	13.2468	+	+

SAMPLE	Sb 0.0186	V 0.0008	B 0.0023	Ba 0.0001	Be 0.0001
82-12	+	0.0020	0.0519	0.0623	+
82-19	+	0.0017	0.0315	0.0060	+
82-20	+	0.0014	0.0615	0.1949	0.0002
82-23	+	+	0.0251	0.2030	0.0002
82-24	+	0.0022	0.0159	0.0903	+
82-28	+	0.0014	0.1209	0.1074	0.0001
82-42	+	0.0032	0.0604	+	+
82-44	+	0.0033	0.0662	0.1051	0.0012
82-7	+	0.0019	0.0314	0.0812	+
83-100	+	0.0021	+	0.1026	0.0001

+ below ICP determination limit

Groundwater Samples Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination Limit		0.0003	0.0178	0.0034	0.0082	0.0020	0.0068	0.0006
83-40	1U	0.0670	*	*	*	0.7694	0.0114	0.1175
83-46	1U	0.0416	0.3920	*	0.0475	0.0818	0.0109	0.0663
83-47	1U	0.0230	0.0224	*	0.0436	0.0055	*	0.1640
83-49	1U	0.0006	*	*	0.0176	0.1620	*	0.0699
83-56	1U	0.0083	*	*	*	0.7128	0.0073	0.0412
83-58	1U	0.0026	0.0185	*	0.0279	0.5116	*	0.0594
83-59	1U	0.0069	0.0230	*	0.0448	0.1218	0.0114	0.0727
83-80	1U	0.0268	*	*	0.0067	0.1351	*	0.5670
83-83	1U	0.0073	0.0402	*	*	0.0818	*	0.0367
83-88	1U	0.0116	*	*	*	0.0126	*	0.0972
83-90	1U	0.0233	0.0729	*	0.0075	0.0537	0.0013	0.2390
83-94	1U	0.0114	*	*	0.0237	0.0247	0.0097	0.0611

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As	Se
	0.0230	0.0012	0.0017	0.0012	0.0016	0.0066	0.0113	0.0212
83-40	*	0.0162	*	0.0015	*	10.2580	*	*
83-46	0.0236	0.0116	*	0.0029	*	15.6020	*	*
83-47	*	0.0241	*	0.0026	*	9.5830	*	*
83-49	*	0.1050	*	0.0017	*	5.5230	*	*
83-56	*	0.0360	*	0.0017	*	13.0250	*	*
83-58	*	0.0918	*	0.0061	*	16.2750	0.0125	*
83-59	*	0.0204	*	0.0038	*	26.4180	*	*
83-80	*	0.0208	*	*	*	52.0000	*	*
83-83	*	0.0180	*	*	*	40.2030	*	*
83-88	*	0.0174	*	*	*	6.0620	*	*
83-90	0.0246	0.0250	*	*	*	32.2950	*	*
83-94	*	0.0275	*	0.0031	*	33.5470	*	*

SAMPLE	Sb	V	B	Ba	Be
	0.0186	0.0008	0.0023	0.0001	0.0001
83-40	*	0.0014	*	0.0391	0.0001
83-46	*	0.0018	*	0.0616	*
83-47	0.0229	0.0030	0.0034	0.0375	*
83-49	*	0.0014	0.0191	0.0173	*
83-56	*	0.0016	0.0172	0.0065	*
83-58	0.0212	0.0024	0.0129	0.0604	*
83-59	*	0.0022	0.0230	0.0722	0.0001
83-80	0.0213	0.0015	0.0006	0.0407	*
83-83	*	0.0017	0.0622	0.0697	*
83-88	*	*	0.0047	0.1005	*
83-90	*	0.0013	0.0130	0.0968	*
83-94	*	0.0017	0.0594	0.0466	*

* below ICP determination limit

Groundwater Samples Duffins Creek-Rouge River Basins Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I++	Br	CO3
83-212	1S	7.30	8.60	67.74	0.15	8.20	0.08	0.00
82-15	1S	7.40	9.75	61.71	0.14	12.00	0.00	0.00
83-106	1S	7.45	8.42	114.64	0.14	3.00	0.12	0.00

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
83-212	317.20	79.05	27.02	14.50	2.50	34.37	+
82-15	475.80	130.30	20.54	22.00	32.00	100.54	0.69
83-106	317.20	125.35	25.52	19.00	1.50	65.31	0.56

+ not determined

++ ug/L

Groundwater Samples Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination Limit		0.0003	0.0178	0.0034	0.0082	0.0020	0.0068	0.0006
82-15	1S	0.0520	0.4621	*	0.0562	0.0288	0.0124	2.4643
83-106	1S	0.0399	*	*	0.0079	0.1830	*	0.6635
83-212	1S	0.0347	*	*	0.0377	0.0020	0.0073	0.1432

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As	Se
	0.0230	0.0012	0.0017	0.0012	0.0016	0.0066	0.0113	0.0212
82-15	*	0.0174	*	0.0039	*	33.5148	0.0176	*
83-106	*	0.0185	*	0.0006	*	21.7698	*	*
83-212	*	0.0089	*	0.0025	*	11.4568	*	*

SAMPLE	Sb	V	B	Ba	Be
	0.0186	0.0008	0.0023	0.0001	0.0001
82-15	*	0.0036	0.0358	0.3705	0.0009
83-106	0.0288	0.0033	0.0038	0.0984	0.0002
83-212	*	0.0035	0.0351	0.1428	0.0002

* below ICP determination limit

Groundwater Samples   Duffins Creek-Rouge River Basins   Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I**	Br	CO3
83-99	1N	7.50	62.99	26.06	0.05	2.20	+	0.00
83-69	1N	7.20	51.21	8.00	0.05	6.00	+	0.00
82-10	1N	7.80	16.61	7.71	0.20	0.00	0.28	0.00
83-103	1N	7.20	97.46	20.34	0.06	0.00	0.60	0.00
82-22	1N	7.25	70.90	20.21	0.10	0.00	0.50	0.00

** ug/L

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
83-99	326.35	105.26	15.23	16.00	1.70	43.64	0.41
83-69	280.60	73.02	15.30	8.50	5.50	56.66	0.49
82-10	286.70	51.93	20.41	6.00	2.50	12.89	0.32
83-103	420.90	139.86	12.68	13.00	3.00	52.05	0.55
82-22	372.10	116.57	13.07	4.80	5.00	35.47	0.53

+ not determined
** ug/L

Groundwater Samples Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination	Limit	0.0003	0.0178	0.0034	0.0082	0.0020	0.0068	0.0006
82-10	1N	0.0113	*	*	0.0462	0.0280	0.0092	0.0564
82-22	1N	0.0007	*	*	0.0263	0.0769	*	0.0682
83-69	1N	0.0145	0.0438	*	0.0072	0.2268	*	*
83-99	1N	0.0006	*	*	0.0228	0.0306	*	0.0411
83-103	1N	0.0009	*	*	0.0110	0.0728	0.0071	0.0457

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As	Se
	0.0230	0.0012	0.0017	0.0012	0.0016	0.0066	0.0113	0.0212
82-10	*	0.0197	*	0.0030	*	4.2983	0.0125	*
82-22	*	0.0329	*	0.0025	*	11.0238	*	*
83-69	*	0.0082	*	*	*	10.0878	*	*
83-99	*	0.0237	*	0.0028	*	14.5478	*	*
83-103	*	0.0205	*	0.0031	*	17.3508	0.0128	*

SAMPLE	Sb	V	B	Ba	Be
	0.0186	0.0008	0.0023	0.0001	0.0001
82-10	*	0.0024	0.0185	0.1082	*
82-22	*	0.0022	*	0.0531	*
83-69	0.0207	0.0012	0.0015	0.0523	*
83-99	*	0.0018	*	0.0528	*
83-103	0.0203	0.0026	0.0168	0.0347	0.0001

* below ICP determination limit

Groundwater Samples Duffins Creek-Rouge River Basins Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I	Br	CO3
83-162	2A	7.40	10.67	10.55	0.11	7.40	0.00	0.00
82-1	2A	7.50	5.85	3.32	0.11	2.80	0.82	0.00
82-34	2A	7.85	7.84	10.42	0.15	0.00.	0.54	0.00

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
83-162	183.00	39.29	14.14	12.50	1.00	2.99	0.25
82-1	250.10	38.50	14.24	10.50	0.80	2.55	0.28
82-34	268.40	42.64	24.40	11.50	2.00	0.74	0.31

+ not determined
** ug/L

Groundwater Samples Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE Determination Limit	Type	Mn 0.0003	P 0.0178	Mo 0.0034	Al 0.0082	Zn 0.0020	Ni 0.0068	Fe 0.0006
82-1	2A	0.0276	0.0273	*	0.0115	0.3687	*	0.0180
82-34	2A	0.0357	0.0976	*	0.0038	0.0974	*	0.6160
83-162	2A	0.0296	0.0288	*	0.0191	0.0074	*	0.2946

SAMPLE	Pb 0.0230	Cu 0.0012	Co 0.0017	Cr 0.0012	Cd 0.0016	S 0.0066	As 0.0113	Se 0.0212
82-1	*	0.0490	*	*	*	0.8498	*	*
82-34	*	0.0069	*	0.0005	*	0.2482	*	*
83-162	*	0.0167	*	*	*	0.9971	*	*

SAMPLE	Sb 0.0186	V 0.0008	B 0.0023	Ba 0.0001	Be 0.0001
82-1	*	0.0010	0.0333	0.1019	*
82-34	*	0.0031	0.0303	0.1106	0.0002
83-162	*	0.0010	0.0213	0.1595	*

* below ICP determination limit

Groundwater Samples Duffins Creek-Rouge River Basins Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I**	br	CO3
83-141	2U	7.35	13.25	16.45	0.08	10.20	0.00	0.00
83-176	2U	7.40	11.87	8.00	0.09	15.00	0.08	0.00
83-164	2U	7.50	15.00	6.00	0.08	7.90	0.40	0.00
83-165	2U	7.33	11.60	9.30	0.11	13.40	0.00	0.00
83-179	2U	7.21	11.03	3.70	0.10	2.80	0.64	0.00
83-196	2U	7.50	6.65		0.14	0.00	0.00	0.00

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
83-141	311.10	41.61	23.97	19.80	0.80	0.66	0.34
83-176	311.10	45.77	15.00	27.00	0.80	1.07	0.30
83-164	280.60	39.35	16.44	19.80	0.80	1.13	0.33
83-165	298.90	44.50	14.51	22.00	0.80	0.96	0.28
83-179	292.80	42.85	16.96	15.00	1.80	1.64	0.32
83-196	366.00	56.00	17.04	11.50		1.26	0.35

* not determined

** ug/L

Groundwater Samples Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination Limit		0.0003	0.0178	0.0034	0.0082	0.0020	0.0068	0.0006
83-141	2U	0.0649	0.1179	*	0.0167	0.0702	*	0.5610
83-164	2U	0.0272	*	*	0.0513	0.0097	*	0.0842
83-165	2U	0.1442	0.0310	*	0.0167	0.0522	*	0.4329
83-176	2U	0.0653	0.0182	*	*	0.0221	*	*
83-179	2U	0.0091	0.0096	*	0.0015	0.0228	*	0.0494
83-196	2U	0.0135	0.0183	*	0.0099	0.0275	*	0.6636

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As	Se
	0.0230	0.0012	0.0017	0.0012	0.0016	0.0066	0.0113	0.0212
83-141	*	0.0391	*	0.0003	*	0.2185	*	*
83-164	*	0.0057	*	*	*	0.3767	*	*
83-165	*	0.0172	*	*	*	0.3190	*	*
83-176	*	0.0168	*	*	*	0.3566	*	*
83-179	*	0.0152	*	*	*	0.5474	*	*
83-196	*	0.0113	*	0.0029	*	0.4200	*	*

SAMPLE	Sb	V	B	Ba	Be
	0.0186	0.0008	0.0023	0.0001	0.0001
83-141	*	0.0018	0.0303	0.1052	*
83-164	*	0.0003	0.0348	0.1530	*
83-165	*	0.0011	0.0280	0.1826	*
83-176	*	0.0007	0.0239	0.1823	*
83-179	*	0.0004	0.0310	0.0040	*
83-196	*	*	*	0.1521	0.0008

* below ICP determination limit

Groundwater Samples   Duffins Creek-Rouge River Basins   Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I	Br	CO3
83-60	3A	7.65	8.55	3.00	0.87	13.20	+	0.00
83-173	3A	7.30	6.50	14.00	0.14	20.00	0.76	0.00
83-175	3A	7.75	6.86	14.17	0.16	12.80	0.10	0.00
83-63	3A	7.50	8.73	3.00	0.10	14.80	+	0.00
83-188	3A	7.15	8.11	13.60	0.12	18.80	0.50	0.00
83-194	3A	7.40	8.19	10.00	0.11	15.20	0.16	0.00

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
83-60	323.30	36.20	15.69	42.00	1.50	1.12	0.36
83-173	225.70	35.17	12.38	33.00	0.80	0.80	0.35
83-175	280.60	45.24	12.40	44.00	0.80	1.99	0.26
83-63	323.30	34.14	14.82	50.50	1.50	1.65	0.34
83-188	286.70	41.78	8.45	42.50	0.80	6.59	0.36
83-194	305.00	33.55	13.80	42.00	1.00	0.78	0.29

+ not determined

++ ug/L

Groundwater Samples   Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination Limit		0.0003	0.0178	0.0034	0.0082	0.0020	0.0068	0.0006
83-63	3A	0.0542	0.3591	+	+	0.0262	+	0.6080
83-60	3A	0.1310	0.1955	+	0.0196	0.0649	+	0.2359
83-173	3A	0.0319	0.0508	+	0.0745	0.2010	+	0.5647
83-175	3A	0.2363	0.1369	0.0037	0.0554	0.0054	+	0.2683
83-188	3A	0.3619	0.1617	0.0143	0.0522	0.0992	+	0.0603
83-194	3A	0.0541	0.1017	+	+	0.0031	+	0.5624

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As	Se
	0.0230	0.0012	0.0017	0.0012	0.0016	0.0066	0.0113	0.0212
83-63	+	0.0134	+	+	+	0.5516	+	+
83-60	+	0.0187	+	+	+	0.3717	+	+
83-173	+	0.0515	+	+	+	0.2669	+	+
83-175	+	0.0617	+	0.0129	+	0.6649	+	+
83-188	+	0.1267	+	+	+	2.1979	+	+
83-194	+	0.0105	+	+	+	0.2587	+	+

SAMPLE	Sb	V	B	Ba	Be
	0.0186	0.0008	0.0023	0.0001	0.0001
83-63	+	0.0013	0.0998	0.0685	+
83-60	+	0.0019	0.0004	0.1756	+
83-173	+	0.0008	0.0473	0.0941	+
83-175	+	0.0008	0.1137	0.7161	+
83-188	+	0.0010	0.0972	0.0544	+
83-194	+	0.0008	0.0839	0.0732	+

+ below ICP determination limit

Groundwater Samples   Duffins Creek-Rouge River Basins   Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I++	Br	CO3
83-171	3U	7.40	6.20	26.99	0.15	1.00	0.00	0.00
83-143	3U	7.71	11.56	5.37	0.08	22.00	0.00	0.00
83-132	3U	7.18	6.87	22.50	+	14.40	0.16	0.00
83-134	3U	7.20	5.01	27.00	+	16.00	0.50	0.00
83-192	3U	7.00	5.67	34.24	+	18.00	0.70	0.00
82-4	3U	8.10	7.04	10.42	0.14	13.60	0.22	0.00
86-1	3U	7.24	4.03	1.63	+	12.50	0.00	0.00
86-2	3U	7.30	5.05	2.90	+	190.00	0.00	0.00

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
83-171	408.70	47.55	16.12	57.50	3.00	1.02	0.45
83-143	231.00	33.57	8.05	40.00	0.50	1.03	0.23
83-132	274.50	41.00	22.50	41.00	1.20	4.50	0.30
83-134	274.50	36.00	23.50	32.50	1.60	1.00	0.38
83-192	280.60	31.00	18.20	52.50	0.70	4.00	0.40
82-4	186.00	23.26	9.69	18.50	3.50	0.04	0.20
86-1	344.65	46.00	14.00	48.50	3.00	2.00	0.42
86-2	341.60	45.50	14.60	53.50	3.75	6.50	0.42

+ not determined
++ ug/L

Groundwater Samples Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination Limit		0.0003	0.0178	0.0034	0.0082	0.0020	0.0068	0.0006
82-4	3U	0.0388	0.0350	*	*	0.0378	*	0.2090
83-132	3U	0.0537	0.0827	*	0.0052	0.1247	*	0.0822
83-134	3U	0.0257	0.0241	*	0.0109	0.0042	*	0.0969
83-143	3U	0.0258	0.1593	0.0088	0.0376	0.0198	*	0.2178
83-171	3U	0.1220	0.2389	*	0.0320	0.0162	0.0118	2.9269
83-192	3U	0.0754	0.1534	*	0.0163	0.1220	*	0.2867

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As	Se
	0.0230	0.0012	0.0017	0.0012	0.0016	0.0066	0.0113	0.0212
82-4	*	0.0076	*	*	*	0.2807	*	*
83-132	*	0.0354	*	*	*	0.2933	*	*
83-134	*	0.0239	*	*	*	0.3575	*	*
83-143	*	0.0225	*	*	*	0.3428	*	*
83-171	*	0.0190	*	0.0049	*	0.3396	*	*
83-192	*	0.0263	*	*	*	0.4062	*	*

SAMPLE	Sb	V	B	Ba	Be
	0.0186	0.0008	0.0023	0.0001	0.0001
82-4	*	*	0.0076	0.1080	*
83-132	*	0.0013	0.0617	0.0685	*
83-134	*	0.0013	0.0519	0.1700	*
83-143	*	0.0009	0.0929	0.0469	*
83-171	*	0.0043	0.0691	0.1549	0.0031
83-192	*	0.0007	0.1013	0.0945	*

* below ICP determination limit

Groundwater Samples Duffins Creek-Rouge River Basins Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I++	Br	CO3
83-160	4A	7.60	3.10	10.30	0.10	10.60	0.30	0.00

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
83-160	317.20	0.41	0.05	121.00	0.00	0.06	0.34

+ not determined
++ ug/L

Groundwater Samples   Duffins Creek-Rouge River Basins
Trace Element Results (mg/L)

SAMPLE	Type	Mn	P	Mo	Al	Zn	Ni	Fe
Determination Limit		0.0003	0.0178	0.0034	0.0082	0.0020	0.0068	0.0006
83-160	4A	*	0.1226	*	0.0042	0.0158	*	0.0033

SAMPLE	Pb 0.0230	Cu 0.0012	Co 0.0017	Cr 0.0012	Cd 0.0016	S 0.0066	As 0.0113	Se 0.0212
83-160	*	0.0303	*	*	*	0.0212	*	*

SAMPLE	Sb 0.0186	V 0.0008	B 0.0023	Ba 0.0001	Be 0.0001
83-160	*	*	*	0.0544	0.0003

* below ICP determination limit

Groundwater Samples Duffins Creek-Rouge River Basins Major and minor ion analysis mg/L

Sample	Type	pH	NO3	Cl	F	I++	Br	CO3
82-11	4U	8.10	7.17	41.69	0.20	30.00	0.34	6.00

Sample	HCO3	Ca	Mg	Na	K	SO4	EC
82-11	231.80	16.30	7.45	80.20	5.00	0.25	0.35

+ not determined
++ ug/L

Potential Contaminants   Major and minor ion analyses

Road De-icing Chemicals

Sample	Description	Location	Source
86040	Road Salt- NaCl	Can. Salt Co. Windsor	Salina Formation
86041	Road Salt- NaCl	Can. Salt Co. Windsor	Salina Formation
86042	Road Salt- CaCl	Allied Chemical	Unknown
85018	Road Salt- NaCl	Can. Salt Co. Windsor	Salina Formation
85019	Road Salt- NaCl	Domtar Goderich Mine	Salina Formation
85020	Road Salt- NaCl	Intl. Mine, Cleveland, Ohio	Salina Formation
85021	Road Salt- NaCl	Estehazy, Saskatchewan	Prairie Formation
85022	Road Salt- NaCl	Can. Salt Co. Windsor	Salina Formation
85023	Road Salt- NaCl	Domtar Goderich Mine	Unknown
85024	Road Salt- NaCl	Int. Mine, Cleveland, Ohio	Unknown
85025	Road Salt- NaCl	Estehazy, Saskatchewan	Prairie Formation

Sample	pH	NO3	Cl	F	I	Br	CO3	HCO3
86040	7.00	120.50	30860.40	0.10	0.02	0.44	0.00	12.20
86041	7.05	125.40	31640.20	0.09	0.02	1.30	0.00	12.20
86042	10.83	91.10	25892.00	1.04	0.07	1.30	90.00	0.00
85018	5.70	64.70	19630.00	0.42	0.02	1.06	0.00	48.00
85019	5.30	62.00	24517.22	0.20	0.02	0.60	0.00	48.80
85020	5.40	67.10	30344.35	0.20	0.01		0.00	48.80
85021	8.10	+	29398.40	0.16	0.01	1.54	0.00	45.75
85022	5.55	98.30	29398.40	0.20	0.02	0.96	0.00	9.15
85023	6.50	93.60	31353.75	0.15	0.02		0.00	42.70
85024	5.80	98.40	28289.10	0.18	0.02	1.01	0.00	36.60
85025	8.90	127.60	28460.55	0.16	0.01	1.60	0.00	48.80

Sample	Ca	Mg	Na	K	SO4	Ec
86040	62.50	5.00	20250.00	13.00	222.00	54.70
86041	140.10	6.00	21500.00	11.50	232.00	53.30
86042	12890.00	1.50	550.00	33.50	25.80	41.20
85018	+	+	+	+	+	88.50
85019	+	+	+	+	+	38.00
85020	+	+	17500.00	250.00	+	54.80
85021	+	+	25500.00	950.00	+	+
85022	+	+	+	+	+	+
85023	+	+	16000.00	25.00	+	57.50
85024	+	+	18000.00	25.00	+	55.00
85025	+	+	21000.00	1687.50	+	57.80

+ not determined

Potential Contaminants: Road Salt Trace element analysis mg/L

Sample Detection Limit	Description	Mn 0.0030	P 0.1785	Mo 0.0340	Al 0.0820	Zn 0.0200	Ni 0.0685
85040	NaCl	*	*	*	166.7000	*	58.9000
85041	NaCl	*	*	*	181.0000	*	42.3000
85042	CaCl	*	*	*	92.1000	*	57.9000

Sample Det. Limit	Fe 0.0060	Pb 0.2300	Cu 0.0150	Co 0.0170	Cr 0.0120	Cd 0.0160	S 0.0660	As 0.1130
85040	58.9000	*	154.6000	*	*	*	82.6000	*
85041	42.3000	*	98.2000	*	*	*	93.6000	*
85042	57.9000	*	252.0000	*	*	*	150.5000	*

Sample Det. Limit	Se 0.2115	Sb 0.1885	V. 0.0008	B 0.0225	Ba 0.0010	Be 0.0010
85040	*	*	*	*	7.4000	*
85041	*	*	*	*	16.0000	*
85042	*	*	*	*	4.9000	*

* below ICP determination limit

Potential Contaminants   Major and minor ion analyses

Sample	Inorganic Fertilizers Description	Location	Source
85026	Mono-Ammonium Phosphate	C.I.L. Courtright, Ont.	Fertilizer Bags
85027	Di-Ammonium Phosphate	C.I.L. Courtright, Ont.	Fertilizer Bags
85028	Prilled Urea	C.I.L. Courtright, Ont.	Fertilizer Bags
85029	Ammonium Nitrate	C.I.L. Courtright, Ont.	Fertilizer Bags

Sample	pH	NO_3	Cl	F	I	Br	CO_3	HCO_3
85026	5.60	221.85	9.80	0.13	0.03	0.65	0.00	3200.00
85027	7.80	357.50	36.00	0.40	0.01	1.08	0.00	1700.00
85028	9.50	25.69	2.13	0.56	0.00	0.29	0.00	121.10
85029	5.80	35393.04	2.40	0.16	0.00	0.18	0.00	18.30

Sample	Ca	Mg	Na	K	SO_4	Ec
85026	0.00	4.75	143.75	31.25	1772.64	393.00
85027	0.00	0.00	112.50	25.00	3220.00	48.10
85028	0.00	2.00	18.75	0.00	4.63	88.70
85029	1.00	0.50	12.50	1.00	2.03	91.00

+ not determined

Potential Contaminants: Fertilizers Trace element analysis mg/L

Sample	Description	Mn	P	Mo	Al	Zn	Ni
Detection Limit		0.0030	0.1785	0.0340	0.0820	0.0200	0.0685
85026	Mono-Ammonium Phosphate	0.0096	8188.6000	0.1176	7.3304	0.1492	0.4065
85027	Di-Ammonium Phosphate	0.1975	+	0.1684	4.8007	0.1766	0.2881
85028	Prilled Urea	0.0036	0.6463	*	*	0.0252	*
85029	Ammonium Nitrate .	0.0133	2.7150	0.0390	1.0320	0.0544	0.0897

Sample	Fe	Pb	Cu	Co	Cr	Cd	S	As
Det. Limit	0.0060	0.2300	0.0150	0.0170	0.0120	0.0160	0.0660	0.1130
85026	0.9302	*	0.1971	0.0478	0.5655	*	590.8800	0.3103
85027	1.1729	*	0.2634	*	0.4291	*	*	0.2982
85028	0.0167	*	0.0762	*	*	*	0.1544	*
85029	0.2091	0.3709	0.1319	0.0541	0.0719	0.0234	0.6763	0.1849

Sample	Se	Sb	V	B	Ba	Be
Det. Limit	0.2115	0.1885	0.0008	0.0225	0.0010	0.0010
85026	*	*	0.2831	0.3172	0.0061	0.0035
85027	*	*	1.5260	0.5109	1.3820	0.0023
85028	*	*	0.0135	*	0.0076	*
85029	0.3592	0.3962	0.0880	0.0567	0.9898	0.0038

* below ICP determination limit

Potential Contaminants Major and minor ion analyses

Sample	Organic Fertilizers Description	Location	Source
85009	Beef Cattle Manure	Glen Becker Farm	Weathered Manure Pile
85032	Chicken Manure Leachate	E. Gwillmbury Twp. Lot 30 Con 7	Liquid Manure Pit
85033	Septic Tank Sludge	Sutton Septic Tank Service	Tap on Truck Tank
85034	Horse Manure Leachate	Stormling Rch. Georgina Twp	Weathered Manure Pile
85035	Pig Manure Leachate	Georgina Twp. Lot 25, Con 2	Liquid Manure Pit
85036	Dairy Cow Manure	Brock Twp. Lot 2 Con 6	Fresh Manure on Spreader
85037	Dairy Cow Manure	Uxbridge Twp. Lot 12, Con 6	Liquid Holding Tank Below Barn
85038	Septic Tank Sludge	Grimsby Ont	Septic Tank
85039	Septic Tank Sludge	Grimsby Ont	Septic Tank

Sample	pH	NO3	Cl	F	I	Br	CO3	HCO3
85009	7.55	+	631.78	0.60	0.46	+	0.00	+
85032	+	7083.57	1200.00	0.36	0.06	+	0.00	+
85033	+	+	227.00	+	0.21	+	0.00	+
85034	+	991.25	179.80	0.18	0.09	+	0.00	+
85035	+	26718.65	268.11	0.26	0.09	+	0.00	+
85036	+	6481.97	277.52	0.21	0.02	+	0.00	+
85037	+	+	7.10	0.14	0.01	+	0.00	237.90
85038	+	+	463.00	+	0.24	+	0.00	+
85039	+	+	247.00	+	0.09	+	0.00	+

Sample	Ca	Mg	Na	K	SO4	Ec
85009	+	+	562.50	312.50	+	5.80
85032	+	+	+	+	+	33.00
85033	+	+	+	+	+	+
85034	+	+	+	+	+	1.90
85035	+	+	+	+	+	17.32
85036	+	+	+	+	+	6.55
85037	+	+	+	+	+	0.36
85038	+	+	+	+	+	+
85039	+	+	+	+	+	+

+ not determined

Potential Contaminants Major and minor ion analyses

Bedrock Waters

Sample	Description	Location	Source
85001	Groundwater	Mountain Rd Landfill Site	Gatehouse Well
85007	Groundwater	S of Grimsby Landfill Site	Domestic Well
85008	Groundwater	Riverside Cedar Park	Tap
85010	Groundwater	Williamburg Twp.	Domestic Well, Ottawa
85011	Groundwater	Williamburg Twp.	Domestic Well, Ottawa
85012	Groundwater	B. Cloyne Domestic	Domestic Well, Bathroom Tap
85013	Formation Water	Dawn Twp. Lambton County	Guelph Fm, Mid-Silurian
85014	Formation Water	Broere Twp.	Dundee Fm, Devonian
85015	Formation Water	Goshewn Twp. Essex County	Eau Claire, Cambrian
85016	Formation Water	Essex County	Trenton Fm, M. Ordovician
85017	Formation Water	Dawn Twp. Lambton County	Salina Fm, U. Silurian
85003	Formation Water	Walker Brothers	Rochester Shale, Mid-Silurian
85005	Formation Water	Glenridge Quarry Landfill	Rochester Shale, Mid-Silurian

Sample	pH	NO3	Cl	F	I	Br	CO3	HCO3
85001	6.45	0.64	70.97	1.15	0.19	0.76	0.00	841.80
85007	6.80	+	966.54	0.75	0.01	0.39	0.00	148.33
85008	7.70	+	226.31	1.42	0.03	0.60	18.00	207.40
85010	7.40	+	28.28	0.46	0.01	0.76	6.00	359.90
85011	+	+	29.01	+	0.00	+	+	+
85012	7.20	+	23.57	0.36	0.01	0.64	9.00	359.90
85013	+	+	229566.04	+	0.01	+	+	+
85014	6.00	+	7609.76	0.60	0.40	1.02	0.00	183.00
85015	5.40	+	130507.04	0.27	10.00	1.06	0.00	18.30
85016	5.80	+	126970.91	0.30	7.81	0.42	0.00	30.50
85017	4.40	+	201889.87	0.15	0.03	0.40	0.00	12.20
85003	6.95	+	23857.00	0.65	0.01	5.70	15.00	127.10
85005	5.75	145.00	66545.00	0.41	7.50	0.38	0.00	73.20

Sample	Ca	Mg	Na	K	SO4	Ec
85001	+	+	68.50	3.00	+	1.81
85007	257.10	113.19	250.00	5.00	134.30	2.52
85008	32.70	21.34	175.00	9.80	171.30	0.95
85010	74.65	30.40	29.00	10.50	76.50	0.59
85011	+	+	+	+	+	+
85012	118.23	12.71	9.80	2.50	31.57	0.55
85013	+	+	+	+	+	+
85014	+	+	3000.00	100.00	+	10.13
85015	+	+	40500.00	2062.50	+	139.70
85016	932.51	995.38	36750.00	1437.50	578.70	126.00
85017	933.70	996.91	80500.00	1650.00	396.87	151.30
85003	+	+	17200.00	312.50	+	70.10
85005	+	+	31750.00	475.00	+	104.20

+ not determined

Potential Contaminants: Bedrock Waters Trace element analysis mg/L

Sample	Description	Mn	P	Mo	Al	Zn	Ni
Detection Limit		0.0030	0.1785	0.0340	0.0020	0.0200	0.0685
85007	Groundwater	0.0469	*	*	0.0508	0.3191	0.0084
85008	Groundwater	*	*	*	0.0404	0.0036	0.0104
85010	Groundwater	2.1414	*	*	0.0425	0.0455	0.0227
85011	Groundwater	4.0031	0.0220	*	0.0888	0.2822	0.0675
85012	Groundwater	*	*	*	0.1095	0.1735	0.0118
85013	Formation Water	0.5054	5.4176	0.0917	2.0760	0.1614	0.2432
85016	Formation Water	1.7240	1.5177	0.0517	1.3069	0.0715	0.1557
85017	Formation Water	0.4348	6.0338	0.0782	1.8832	0.1633	0.2173
85005	Formation Water	0.8664	1.0658	0.0421	0.9628	5.7774	0.1218

Sample	Fe	Pb	Cu	Co	Cr	Cd	S	As
Det. Limit	0.0060	0.2300	0.0150	0.0170	0.0120	0.0160	0.0660	0.1130
85007	0.0548	*	*	*	*	*	44.7670	*
85008	0.0453	*	*	*	*	*	57.1280	*
85010	0.0426	*	*	*	*	*	25.5250	*
85011	15.8170	*	*	*	*	*	27.6440	0.3320
85012	0.0488	*	*	*	*	*	10.5240	*
85013	3.3465	1.1153	16.1820	0.1406	0.1972	0.0692	154.4100	1.4011
85016	2.4999	0.6515	1.8804	0.0809	0.1212	0.0422	192.9000	0.8266
85017	7.4969	1.1090	3.5434	0.1254	0.1793	0.0671	132.2900	1.1852
85005	0.1860	0.4918	3.3964	0.0599	0.0951	0.0457	478.9600	0.5185

Sample	Se	Sb	V	B	Ba	Be
Det. Limit	0.2115	0.1885	0.0008	0.0225	0.0010	0.0010
85007	*	*	*	*	0.3483	*
85008	*	*	*	0.7332	0.0156	*
85010	*	*	*	0.1211	0.0602	*
85011	*	*	*	6.1933	0.4176	0.0027
85012	*	*	*	*	0.0637	*
85013	0.8072	3.1327	0.2398	6.5401	0.2237	0.0090
85016	0.5079	2.2086	0.1486	9.8370	0.3418	0.0052
85017	0.7444	2.6789	0.2175	6.8594	0.0240	0.0088
85005	0.3697	1.2972	0.1141	1.5597	0.1254	0.0036

* below ICP determination limit

Potential Contaminants Major and minor ion analyses

Landfill Leachates

Sample	Description	Location	Source
85002	Landfill Leachate	Mountain Rd Landfill Site	Leachate Collection Manhole
85004	Landfill Leachate	Glenridge Quarry Landfill	Leachate Collection Manhole
85006	Landfill Leachate	Grimsby Landfill Site	Leachate Pond
85030	Landfill Leachate	Brock West Landfill	Leachate Collection System
85031	Landfill Leachate	Brock West Landfill	Leachate Collection System

Sample	pH	NO3	Cl	F	I	Br	CO3	HCO3
85002	7.15	26.58	499.77	0.95	0.24	+	0.00	1700.00
85004	7.20	+	685.10	0.76	0.17	+	0.00	+
85006	7.05	+	400.00	2.34	0.02	+	0.00	1860.50
85030	+	103.40	661.74	0.28	+	+	0.00	+
85031	+	123.59	676.10	0.26	+	+	0.00	+

Sample	Ca	Mg	Na	K	SO4	Ec
85002	+	+	300.00	37.50	+	3.62
85004	+	+	650.00	337.50	+	6.49
85006	+	+	+	+	+	7.23
85030	+	+	+	+	+	8.96
85031	+	+	+	+	+	8.97

+ not determined

Potential Contaminants: Landfill leachates   Trace element analysis mg/L

Sample	Description	Mn	P	Mo	Al	Zn	Ni
Detection Limit		0.0030	0.1785	0.0340	0.0820	0.0200	0.0685
85002	Landfill Leachate	*	0.3822	*	*	0.0239	*

Sample	Fe	Pb	Cu	Co	Cr	Cd	S	As
Det. Limit	0.0060	0.2300	0.0150	0.0170	0.0120	0.0160	0.0660	0.1130
85002	0.0286	*	*	*	*	*	149.1000	0.1140

Sample	Se	Sb	V	B	Ba	Be
Det. Limit	0.2115	0.1885	0.0008	0.0225	0.0010	0.0010
85002	*	*	*	1.4552	0.1098	*

* below ICP determination limit

Major and Minor ion analysis mg/L

Urban Road Sample No.	Lithology	Location	Depth (m)	pH	NO3
2B	lgt brn-orng sand	Millwood Rd Bridge	0.43	7.75	43.41
3A	lgt brn-orng sand	"	0.30	8.45	157.30
3B	sand & gravel	"	1.35	8.10	80.63
4A	lgt brn-orng sand	"	0.30	7.95	120.47
4B	sand & gravel	"	1.35	8.10	110.75
6A	lgt brn sand	"	1.35	7.50	110.75
6B	lgt brn sand	"	2.05	7.45	60.67
7A	lgt brn sand	"	0.62	6.25	80.60
7B	lgt brn sand	"	1.34	7.30	73.10
7C	lgt brn sand	"	2.10	7.25	55.38
7E	lgt brn sand	"	3.29	7.70	46.52
9A	brn sand & gravel	Millwood Rd Bridge	0.71	8.10	183.85
9B	brn sand & gravel	"	1.38	7.55	95.25
9C	brn sand & gravel	"	1.87	7.70	110.75
9D	brn sand & gravel	"	2.65	7.70	106.32
23A	lgt brn sand	Don Valley Prkwy Ramp	1.21	+	91.40
23B	lgt brn sand	"	2.32	+	61.60

SAMPLE	Cl	F	CO3	HCO3	Br	I	Na+
2B	865.05	0.48	+	+	0.58	+	+
3A	466.01	1.24	+	+	0.10	+	+
3B	3230.91	0.34	30.00	549.00	0.46	+	+
4A	2537.20	0.92	+	+	0.25	+	785.00
4B	1793.40	0.30	+	+	+	0.02	+
6A	8543.17	0.16	0.00	146.40	+	0.01	3400.00
6B	13721.10	0.14	+	+	+	0.04	+
7A	+	0.09	+	+	+	+	+
7B	3966.00	+	+	+	+	+	8250.00
7C	6785.90	0.12	0.00	134.20	+	+	4400.00
7E	3896.50	0.08	+	+	+	0.02	3105.00
9A	2838.84	0.68	+	+	+	+	3420.00
9B	9825.61	0.30	+	+	0.58	+	4920.00
9C	8000.01	0.26	+	+	0.57	+	5340.00
9D	5652.86	0.21	36.00	585.60	0.16	0.01	+
23A	269.92	+			0.05	0.01	270.00
23B	2994.10	+	0.00	213.50	0.05	0.00	1900.00

Urban Road

SAMPLE	K+	Mg++	Ca++	SO4	Ec
2B	+	5.07	43.05	159.69	+
3A	+	+	+	132.65	2.68
3B	+	1.62	54.42	+	7.40
4A	21.50	+	+	+	2.64
4B	+	+	+	121.78	+
6A	19.50	+	+	+	16.80
6B	20.00	34.32	1065.32	515.06	29.60
7A	+	+	+	+	+
7B	13.50	+	+	+	13.44
7C	11.50	21.75	721.54	364.63	17.50
7E	8.75	17.38	429.20	343.95	11.61
9A	19.50	0.90	35.26	118.46	7.34
9B	+	13.98	551.11	325.41	+
9C	+	13.98	451.72	593.64	18.06
9D	35.50	11.92	280.38	244.93	11.60
23A	2.00	0.00	110.00	230.00	+
23B	6.50	6.00	190.00	600.00	+

+ not determined

Auger Site: Urban Road

Sample No.	Mn	P	Mo	Al	Zn	Ni	Fe
Det. Limit	0.0030	0.1785	0.0340	0.0020	0.0200	0.0685	0.0060
2B	0.1683	1.2766	0.0678	6.0593	0.0488	*	17.0479
3B	0.0282	0.5891	*	1.9596	0.0652	*	5.0391
4B	0.0114	0.3289	*	0.0655	*	*	1.7516
5A	0.0778	0.2951	*	0.1063	0.0326	*	0.0012
5B	0.0784	*	*	0.1031	0.0552	*	0.0280
6B	0.2981	0.2165	*	0.2104	0.0291	*	0.0385
7C	0.0235	*	*	0.1291	0.0278	*	0.0290
7D	*	*	*	*	0.0370	*	0.0751
7E	0.1566	*	*	*	0.0278	*	0.0387
9A	0.2528	1.2623	*	4.0468	0.1778	*	26.0389
9B	0.0376	0.2566	*	0.1112	0.0332	*	0.0394
9C	0.0300	0.1815	*	0.0068	0.0339	*	0.0098
9D	0.0183	0.2159	*	*	0.4995	*	0.0148

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As
Det. Limit	0.2300	0.0150	0.0170	0.0120	0.0160	0.0660	0.1130
2B	*	0.2545	*	0.0496	*	53.3320	*
3B	*	0.0512	*	0.0196	*	44.3020	*
4B	*	0.0388	*	*	*	40.6740	*
5A	*	0.0172	*	*	*	104.0300	0.1323
5B	*	0.1678	*	*	*	93.7810	*
6B	*	0.0197	*	0.0147	*	171.9400	*
7C	*	0.2359	*	*	*	121.7300	*
7D	*	0.1797	*	0.0160	*	112.3900	*
7E	*	0.2054	*	*	*	114.0300	*
9A	0.3421	0.2004	*	0.0315	*	39.5640	*
9B	*	0.3494	*	*	*	100.6400	*
9C	*	0.2307	*	*	*	198.1700	*
9D	1.8700	0.1711	*	*	*	81.7760	*

SAMPLE	Se	Sb	V	B	Ba	Be
Det. Limit	0.2115	0.1885	0.0008	0.0225	0.0010	0.0010
2B	0.1022	0.1194	0.0484	0.0979	0.0730	0.0038
3B	0.0796	0.0476	0.0123	0.0717	0.0895	0.0037
4B	0.0757	0.0541	0.0044	0.0455	0.0715	0.0016
5A	0.0703	0.0576	0.0064	0.0326	0.1973	0.0003
5B	0.0664	0.0762	0.0047	0.0386	0.3964	0.0003
6B	0.0695	0.1793	0.0171	0.0357	0.6715	0.0005
7C	0.0742	0.1142	0.0085	0.0334	0.5167	0.0003
7D	0.0487	0.0789	0.0037	0.0293	0.2575	0.0002
7E	0.0564	0.0748	0.0032	0.1525	0.3364	0.0001
9A	0.0811	0.0755	0.0572	0.0608	0.1916	0.0205
9B	0.0873	0.0877	0.0045	0.0855	0.5795	0.0002
9C	0.0757	0.0798	0.0019	0.1485	0.3142	0.0002
9D	0.1244	0.0326	*	0.2265	0.2914	*

* below ICP determination limits

Major and Minor ion analysis mg/L

Snow Dump Sample No.	Lithology	Location	Depth (m)	pH	NO3
8A	blk sand & gravel	Snow Dump Don Valley	0.34	6.55	830.63
8B	blk sand & gravel	"	0.45	6.55	+
19A	drk brn-blk sand	Snow Dump, Don Valley	Surface	+	+
20A	drk brn-blk sand	"	Surface	+	226.80
21A	drk brn-blk sand	"	0.25	+	72.70
21B	drk brn-blk sand	"	0.38	+	40.20
21C	drk brn-blk sand	"	0.63	+	+
22A	drk brn sand	"	0.23	+	86.80
22B	drk brn sand	"	0.34	+	+

SAMPLE	Cl	F	CO3	HCO3	Br	I	Na+
8A	192.84	1.20	+	+	+	+	+
8B	+	0.85	+	+	0.56	+	+
19A	+	+	+	+	+	+	+
20A	1363.00	+	+	+	0.12	0.00	1130.00
21A	33.62	+	+	+	0.20	0.00	180.00
21B	33.61	+	+	+	0.20	0.00	180.00
21C	+	+	+	+	+	+	+
22A	40.00	+	+	+	0.15	0.00	130.00
22B	789.75	+	+	+	0.20	0.00	1160.00

SAMPLE	K+	Mg++	Ca++	SO4	Ec
8A	+	2.56	28.21	185.54	+
8B	+	+	+	+	+
19A	+	+	+	+	+
20A	20.00	9.25	60.00	600.00	+
21A	0.00	2.50	46.00	97.00	+
21B	2.00	2.25	26.50	130.00	+
21C	+	+	+	+	+
22A	11.00	4.50	13.00	385.00	+
22B	16.20	46.50	9.25	+	+

+ not determined

Auger Site: Snow Dump

Sample No.	Mn	P	Mo	Al	Zn	Ni	Fe
Det. Limit	0.0030	0.1785	0.0340	0.0020	0.0200	0.0685	0.0060
8A	0.6012	2.4199	*	17.8170	0.4995	*	61.9589
21B	0.0050	0.4500	*	*	0.0244	*	0.7997
22B	0.0036	0.3626	*	0.1053	0.0206	*	0.1913

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As
Det. Limit	0.2300	0.0150	0.0170	0.0120	0.0160	0.0660	0.1130
8A	1.0700	0.5860	*	0.0713	0.0126	61.9600	*
21B	*	0.0782	*	*	*	140.0600	*
22B	*	0.0663	*	*	*	162.3000	*

SAMPLE	Se	Sb	V	B	Ba	Be
Det. Limit	0.2115	0.1885	0.0008	0.0225	0.0010	0.0010
8A	0.0871	0.0846	0.1443	0.2334	0.2535	0.0130
21B	*	*	*	0.0872	0.0893	*
22B	*	*	*	0.0462	0.1182	*

* below ICP determination limits

Interstitial Water Sample Results Major and Minor ion analysis mg/L

Urban Park Sample No.	Lithology	Location	Depth (m)	pH	NO3
1A	lgt brn sand	Seton Park, Don Valley	0.30	7.75	12.40
1B	lgt brn sand	"	0.60	7.70	11.96
1C	lgt brn sand	"	0.90	7.35	12.63
1D	lgt brn sand	"	1.20	7.50	50.95

SAMPLE	Cl	F	CO3	HCO3	Br	I	Na+
1A	54.98	0.13	60.00	366.00	1.96	+	+
1B	59.98	0.12	75.00	350.75	+	+	+
1C	54.98	0.13	30.00	335.50	0.17	0.01	+
1D	52.11	+	+	+	+	+	36.50

SAMPLE	K+	Mg++	Ca++	SO4	Ec
1A	+	21.80	106.63	66.32	+
1B	+	20.36	108.82	53.21	+
1C	+	18.22	95.95	74.62	0.56
1D	5.00	13.04	64.51	63.68	+

+ not determined

Intersitial Water Sample Results Trace Constituents

Auger Site: Urban Park

Sample No.	Mn	P	Mo	Al	Zn	Ni	Fe
Det. Limit	0.0030	0.1785	0.0340	0.0820	0.0200	0.0685	0.0060
1A	+	0.2497	+	+	+	+	0.0121
1B	0.0971	+	+	+	0.0207	+	0.0326
1C	+	+	+	+	+	+	0.0326
1D	+	+	+	+	0.0245	+	0.0195
10A	0.0389	+	+	+	+	+	0.0537
10B	1.0448	+	+	+	+	+	0.1280

NO <

Major + minor

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As
Det. Limit	0.2300	0.0150	0.0170	0.0120	0.0160	0.0660	0.1130
1A	+	+	+	+	+	22.1310	+
1B	+	+	+	+	+	17.7840	+
1C	+	+	+	+	+	24.9320	+
1D	+	0.0725	+	+	+	21.2520	+
10A	+	0.0016	+	+	+	34.1500	+
10B	+	0.0142	+	+	+	3.5721	+

SAMPLE	Se	Sb	V	B	Ba	Be
Det. Limit	0.2115	0.1885	0.0008	0.0225	0.0010	0.0010
1A	0.0502	0.0526	0.0039	0.0648	0.0629	0.0001
1B	0.0618	0.0312	0.0045	0.0923	0.0774	0.0001
1C	0.0517	0.0319	0.0040	0.1279	0.0691	0.0001
1D	0.0394	0.0512	0.0027	0.0313	0.0310	0.0001
10A	0.0742	0.0548	0.0007	0.1068	0.0855	0.0001
10B	0.0935	0.0297	+	0.1205	0.0941	+

+ below ICP determination limits

Major and Minor ion analysis mg/L

Rural Road Sample No.	Lithology	Location	Depth (m)	pH	NO3
14A	lgt brn sand	Ballantrae, Ont.	0.30	7.42	29.45
14B	drk brn sand	"	0.90	7.27	21.70
14C	drk brn sand	"	1.87	7.37	49.12
14E	rsty brn sand	"	3.67	7.45	26.66
15A	lgt brn sand	"	0.30	7.55	28.17
15B	lgt brn sand	"	0.97	7.65	25.73
15C	rsty brn sand	"	1.70	7.65	+
15D	rsty brn sand	"	1.82	7.50	30.16
15E	rsty brn sand	"	2.29	7.77	+
15F	brn sand	"	2.70	7.30	16.87

SAMPLE	Cl	F	CO3	HCO3	Br	I	Na+
14A	17.54	0.06	15.00	137.25	+	+	27.00
14B	8.41	0.06	+	+	+	+	27.50
14C	15.87	0.06	+	+	0.30	0.01	30.00
14E	36.84	0.03	+	268.40	0.70	0.01	30.00
15A	25.15	0.06	+	+	+	+	30.00
15B	12.30	0.04	+	+	0.10	0.01	+
15C	27.21	+	+	+	+	+	32.50
15D	72.89	0.06	+	+	+	+	+
15E	92.70	+	+	+	+	+	65.00
15F	162.68	0.02	+	237.90	0.56	+	90.50

SAMPLE	K+	Mg++	Ca++	SO4	Ec
14A	5.00	+	+	+	0.31
14B	5.00	+	+	+	+
14C	5.00	+	+	+	+
14E	2.00	+	+	+	0.40
15A	4.50	+	+	+	0.31
15B	+	+	+	+	+
15C	1.00	0.76	21.84	23.71	+
15D	+	2.13	69.22	32.39	0.41
15E	1.00	+	+	+	+
15F	1.00	+	+	+	0.54

+ not determined

Auger Site: Rural Road

Sample No.	Mn	P	Mo	Al	Zn	Ni	Fe
Det. Limit	0.0030	0.1785	0.0340	0.0020	0.0200	0.0685	0.0060
14D	+	+	+	+	+	+	+
14F	0.0036	+	+	+	0.0283	+	+
15C	0.0121	0.1853	+	0.1137	0.0492	+	0.0176
15D	+	+	+	+	+	+	+
16C	0.0044	0.2388	+	+	0.0255	+	+

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As
Det. Limit	0.2300	0.0150	0.0170	0.0120	0.0160	0.0660	0.1130
14D	+	+	+	+	+	3.8533	+
14F	+	+	+	+	+	4.2891	+
15C	+	0.3349	+	+	+	7.9454	+
15D	+	+	+	+	+	10.0410	+
16C	+	0.0144	+	+	+	9.2275	+

SAMPLE	Se	Sb	V	B	Ba	Be
Det. Limit	0.2115	0.1885	0.0008	0.0225	0.0010	0.0010
14D	0.0476	0.0328	0.0035	+	0.0030	+
14F	0.0674	0.0368	0.0057	0.0255	0.0053	0.0001
15C	0.0197	0.0518	0.0026	+	0.0099	+
15D	0.0395	0.0334	0.0013	+	0.0049	+
16C	+	+	+	0.0447	0.0188	+

+ below ICP determination limits

Major and Minor ion analysis mg/L

Fallow Field

Sample No.	Lithology	Location	Depth (m)	pH	NO3
11A	lgt brn clay	Milliken, Ont	0.91	7.55	297.25
11B	lgt brn clay	"	1.45	7.60	98.79
11C	lgt brn clay	"	2.27	7.55	40.31
12A	lgt brn clay	"	1.08	7.82	40.31
12B	lgt brn clay	"	1.58	+	+
12C	lgt brn clay	"	2.15	8.07	69.46
13A	lgt brn clay	"	0.71	7.10	136.84
13B	lgt brn clay	"	1.45	7.80	63.08

SAMPLE	Cl	F	CO3	HCO3	Br	I	Na+
11A	+	0.11	+	+	+	+	+
11B	+	0.10	+	+	0.72	0.01	+
11C	104.00	0.11	+	+	+	+	270.00
12A	584.60	+	+	+	+	+	175.00
12B	+	+	+	207.40	+	+	260.00
12C	245.87	+	+	+	+	+	285.00
13A	216.80	+	+	+	+	0.00	+
13B	346.11	0.05	+	+	0.88	0.01	285.00

SAMPLE	K+	Mg++	Ca++	SO4	Ec
11A	+	+	+	+	+
11B	+	12.74	101.71	74.95	+
11C	+	+	+	112.39	+
12A	+	+	+	+	+
12B	3.00	10.02	60.24	+	1.57
12C	+	+	+	42.26	+
13A	+	+	+	+	+
13B	3.50	19.02	152.30	67.27	1.97

+ not determined

Auger Site: Fallow Field

Sample No.	Mn	P	Mo	Al	Zn	Ni	Fe
Det. Limit	0.0030	0.1785	0.0340	0.0020	0.0200	0.0685	0.0060
11B	0.0067	*	*	*	*	*	0.0006
12A	0.0068	*	*	*	0.0244	*	0.0163
12C	0.0176	0.2199	*	0.2242	0.0768	*	0.1167

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As
Det. Limit	0.2300	0.0150	0.0170	0.0120	0.0160	0.0660	0.1130
11B	*	0.0369	*	*	*	25.0420	*
12A	*	0.0139	*	*	*	37.5440	*
12C	*	0.4094	*	*	*	14.1360	*

SAMPLE	Se	Sb	V	B	Ba	Be
Det. Limit	0.2115	0.1885	0.0008	0.0225	0.0010	0.0010
11B	0.0432	0.0569	0.0032	*	0.0539	0.0001
12A	0.0201	0.0451	0.0028	*	0.0466	0.0001
12C	0.0174	0.0500	0.0027	0.0402	0.0437	*

* below ICP determination limits

Major and Minor ion analysis mg/L

Cropland Sample No.	Lithology	Location	Depth (m)	pH	NO3
16A	lgt brn clay	Markham cornfield	0.27	+	379.50
16B	lgt brn clay	"	0.34	+	166.57
16C	lgt brn clay	"	0.54	+	130.69
16D	lgt brn clay	"	0.74	+	126.83
16E	lgt brn clay	"	0.93	+	35.13
25A	lgt brn sand	Jerseyville cornfield	0.35	+	128.50
25B	lgt brn sand	"	0.55	+	63.30
25C	lgt brn sand	"	0.77	+	51.80
25D	lgt brn sand	"	0.90	+	67.30
26A	lgt brn sand	"	0.22	+	209.10
26B	brn sand & clay	"	0.49	+	192.26
27A	lgt brn sand	"	0.23	+	50.10
27B	sand with clay	"	0.68	+	78.40

SAMPLE	Cl	F	CO3	HCO3	Br	I	Na+
16A	16.70	+	+	+	+	+	11.00
16B	23.92	+	+	+	+	+	12.00
16C	59.98	+	+	+	+	+	11.00
16D	21.85	+	+	+	+	+	15.50
16E	63.96	+	+	+	+	+	5.50
25A	35.12	0.09	+	30.50	0.47	0.00	5.20
25B	33.50	0.08	+	18.30	0.65	0.00	4.30
25C	21.40	0.08	+	18.30	0.54	0.01	10.00
25D	32.50	0.08	+	12.20	0.70	0.01	7.25
26A	27.40	0.07	+	18.30	0.15	0.01	11.00
26B	32.60	0.08	+	12.20	0.15	0.01	12.00
27A	99.75	0.08	+	12.20	0.28	0.01	17.00
27B	+	0.08	+	+	0.29	0.01	15.20

SAMPLE	K+	Mg++	Ca++	SO4	Ec
16A	2.80	5.50	55.00	+	+
16B	0.00	4.75	40.00	+	+
16C	0.30	4.25	72.00	52.00	+
16D	3.30	4.50	40.00	35.00	+
16E	1.00	2.00	117.50	+	+
25A	3.30	4.50	65.00	8.00	+
25B	1.00	2.50	42.00	15.00	+
25C	2.10	3.75	41.00	30.00	+
25D	4.30	5.25	46.00	55.00	+
26A	3.50	7.25	65.20	55.00	+
26B	0.80	9.50	116.00	11.00	+
27A	12.30	7.25	77.50	15.00	+
27B	2.70	6.00	60.00	11.00	+

+ not determined

Auger Site: Crooland

Sample No.	Mn	P	Mo	Al	Zn	Ni	Fe
Det. Limit	0.0030	0.1785	0.0340	0.0020	0.0200	0.0685	0.0060
25A	0.0312	0.2412	+	0.1334	0.0983	+	0.1440
25B	0.0050	0.2258	+	+	0.0328	+	+
25C	0.0148	+	+	+	0.0382	+	0.0382
25D	0.0514	0.2770	+	+	0.0899	+	0.1232

SAMPLE	Pb	Cu	Co	Cr	Cd	S	As
Det. Limit	0.2300	0.0150	0.0170	0.0120	0.0160	0.0660	0.1130
25A	+	0.0214	+	+	+	4.5700	+
25B	+	0.0194	+	+	+	5.2259	+
25C	+	0.0218	+	+	+	7.0107	+
25D	+	0.0149	+	+	+	4.6810	+

SAMPLE	Se	Sb	V	B	Ba	Be
Det. Limit	0.2115	0.1885	0.0008	0.0225	0.0010	0.0010
25A	+	+	+	0.0366	0.0391	+
25B	+	+	+	0.0385	0.0090	+
25C	+	+	+	0.0339	0.0168	+
25D	+	+	+	0.0247	0.1659	+

+ below ICP determination limits

Sediment Analysis

Neutron Activation Analysis

Sample	Parameter ug/g Mn	Cl	Ca
Cropland 17A	0.10	0.62	19.36
Cropland 17B	0.08	3.70	115.45
Cropland 18D	0.07	5.15	160.84
Cropland 16C	0.06	6.28	196.18
Cropland 17C	0.07	5.10	159.06
Cropland 17D	0.07	5.16	160.93
Cropland 16E	0.06	5.28	164.83
Cropland 16B	0.13	0.59	18.38

Sediment Analysis
Neutron Activation Analysis

Parameter
ug/g

Sample	La	Sc	Fe	Na	Co	Cr
Snow Dump	18.53	6.88	2.71	1.20	8.71	40.29
Cropland 16C	15.95	4.66	1.34	0.68	5.17	23.13
Urban Road 9a	13.30	5.35	1.66	1.57	5.05	26.29
Cropland 15C	15.30	4.44	1.37	1.79	4.39	28.89
Snow Dump 22A	13.67	6.73	2.15	1.73	6.88	38.79
Cropland 25A	16.02	6.49	2.29	1.57	6.73	28.11

Sediment Analysis
Neutron Activation Analysis

Parameter
ug/g

Sample	Ba	Ti	Mg	Na	V	Al/P
Rural Road 15C	0.34	0.84	7.93	16.43	0.03	46.02
Urban Road 9A	0.41	0.98	9.26	14.09	0.03	45.13
Snow Dump 21B	0.33	1.23	11.16	9.50	0.06	52.53
Snow Dump 21A	0.41	0.96	9.96	14.17	0.04	43.44
Snow Dump 22A	8.46	1.48	8.50	16.58	0.04	51.67
Snow Dump 22B	0.47	0.87	10.66	17.34	0.03	50.69
Snow Dump 20B	0.24	0.87	6.16	0.69	0.00	12.77
Snow Dump 21C	0.45	1.27	13.92	9.27	0.05	46.30
Snow Dump 20A	0.48	1.49	10.60	11.51	0.04	45.56
Snow Dump 21D	2.05	1.06	15.59	9.52	0.06	49.11
Snow Dump	0.32	0.98	12.72	9.97	0.04	37.51
Cropland 16B	0.42	1.67	16.53	10.72	0.08	72.31
Cropland 18B	0.40	1.14	13.93	6.13	0.07	56.58
Cropland 18C	0.30	0.96	12.26	4.75	0.06	50.35
Cropland 16A	0.39	1.53	13.18	11.19	0.07	66.53
Cropland 16D	0.23	4.28	21.29	7.87	0.08	37.58

Sediment Analysis

Neutron Activation Analysis

	Parameter mg/g		
Sample	Mn	Cl	Ca
Rural Road 15C	0.04	0.20	94.50
Urban Road 9A	0.05	0.12	59.68
Snow Dump 21B	0.08	0.31	102.75
Snow Dump 21A	0.07	0.14	64.65
Snow Dump 22A	0.07	0.04	52.19
Snow Dump 22B	0.05	0.73	57.11
Snow Dump 20B	0.20	0.00	56.86
Snow Dump 21C	0.07	0.68	102.29
Snow Dump 20A	0.20	0.13	102.77
Snow Dump 21D	0.08	0.37	96.68
Snow Dump	0.09	0.67	127.16
Cropland 16B	0.10	0.15	14.39
Cropland 18B	0.07	0.09	131.35
Cropland 18C	0.06	0.11	168.12
Cropland 16A	0.09	0.17	21.14
Cropland 16D	0.05	0.04	211.81

Sediment Analysis
Neutron Activation Analysis

Parameter
ug/g

Sample	Ba	Ti	Mg	Na	V	Al/P
Cropland 17A	0.52	1.63	15.68	10.22	0.08	71.95
Cropland 17B	0.35	1.23	13.20	8.14	0.06	54.66
Cropland 18D	0.35	0.89	13.43	5.72	0.06	49.37
Cropland 16C	0.23	1.02	8.58	6.95	0.03	32.94
Cropland 17C	0.32	1.30	13.78	5.51	0.06	51.41
Cropland 17D	0.36	1.24	14.66	4.83	0.06	50.78
Cropland 16E	0.23	0.87	10.26	8.31	0.04	38.38
Cropland 16B	0.49	1.39	15.13	11.92	0.07	69.79

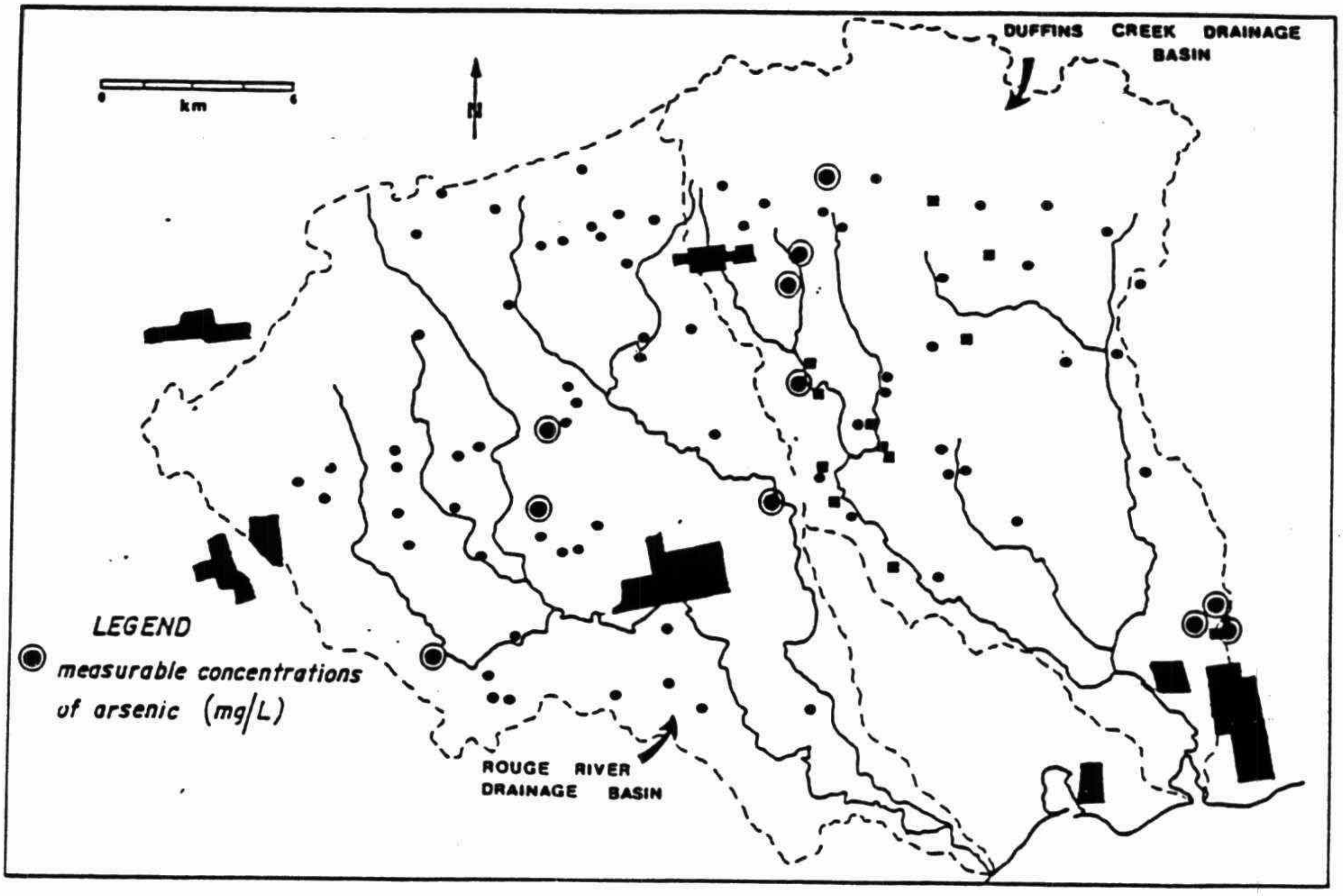

DUFFINS CREEK DRAINAGE BASIN
0
km
6
N
LEGEND
measurable concentrations of arsenic (mg/L)
ROUGE RIVER DRAINAGE BASIN

Figure VI.1 Distribution of arsenic, Duffins Creek-Rouge River basins

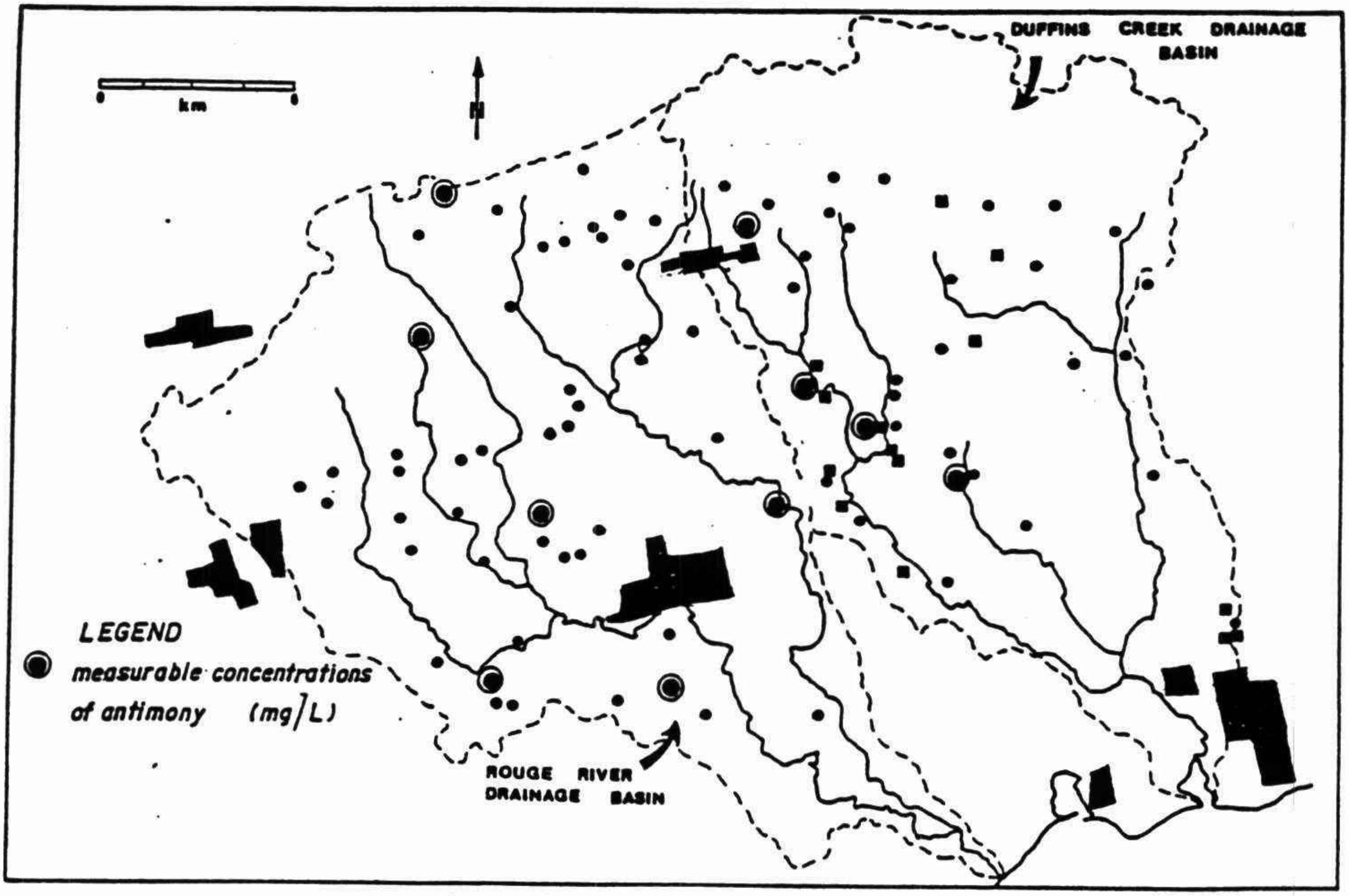

DUFFINS CREEK DRAINAGE BASIN
km
N
LEGEND
◉ measurable concentrations of antimony (mg/L)
ROUGE RIVER DRAINAGE BASIN

Figure VI.2 Distribution of antimony, Duffins Creek-Rouge River basins

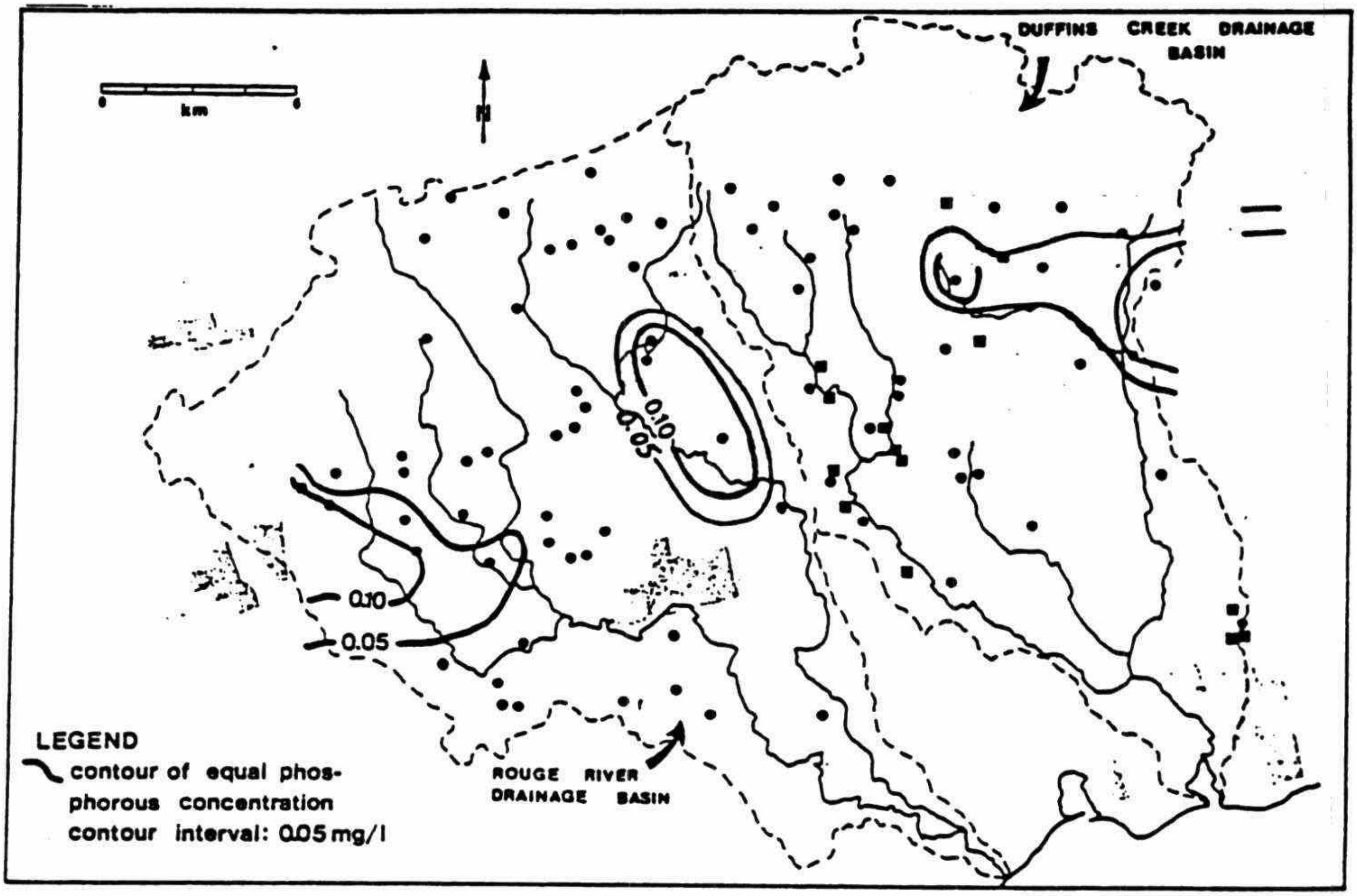

DUFFINS CREEK DRAINAGE BASIN
0
km
6
N
0.10
0.05
0.10
0.05
ROUGE RIVER DRAINAGE BASIN
LEGEND
contour of equal phosphorous concentration
contour interval: 0.05 mg/l

Figure VI- 3 Distribution of phosphorous, Duffins Creek-Rouge River basins

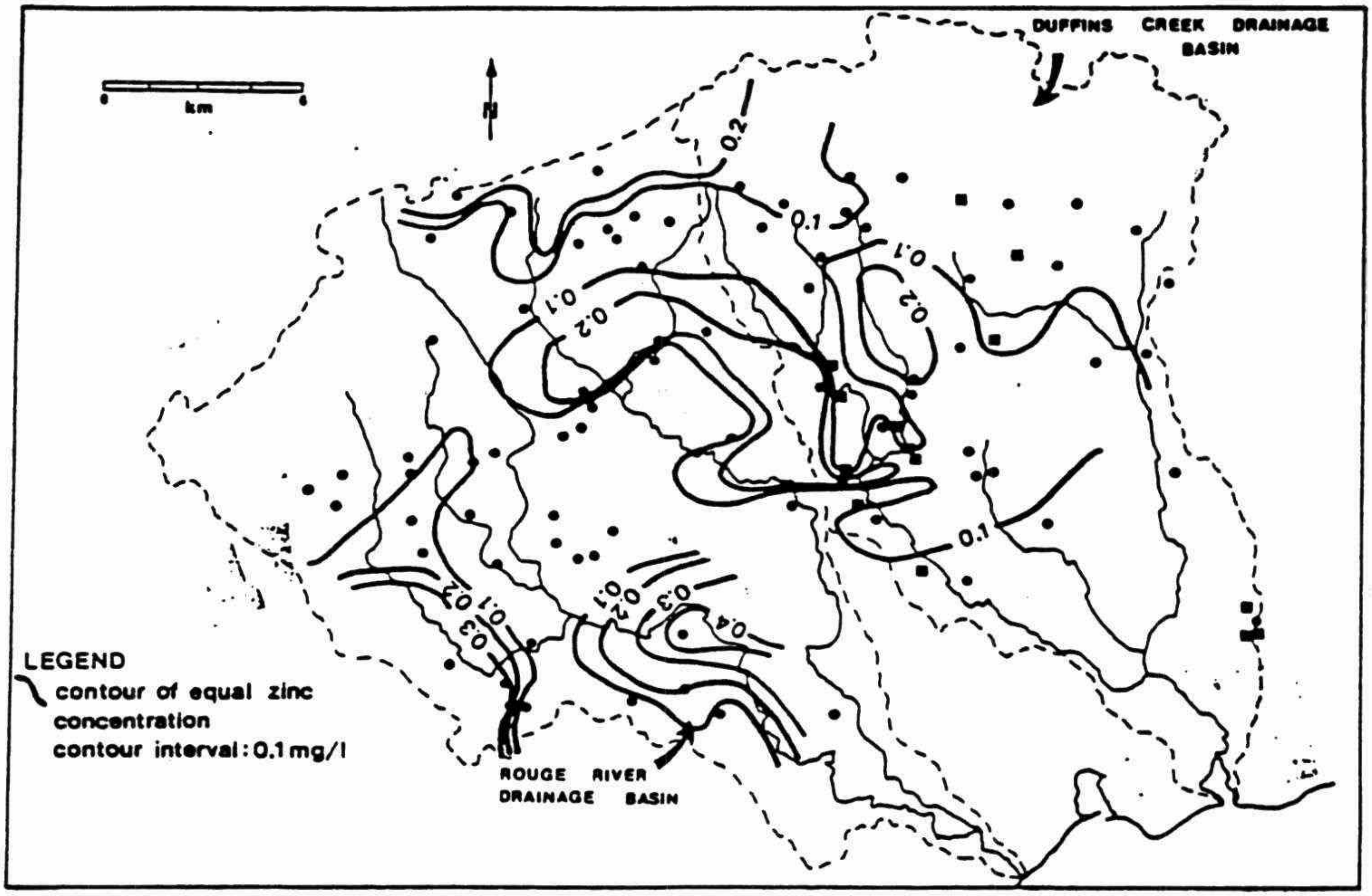

DUFFINS CREEK DRAINAGE BASIN
0
km
6
N
0.2
0.1
0.1
0.2
0.1
0.2
0.1
0.1
0.2
0.3
0.1
0.2
0.3
0.4
LEGEND
contour of equal zinc concentration
contour interval: 0.1 mg/l
ROUGE RIVER DRAINAGE BASIN

Figure VI-4 Distribution of zinc, Duffins Creek-Rouge River basins

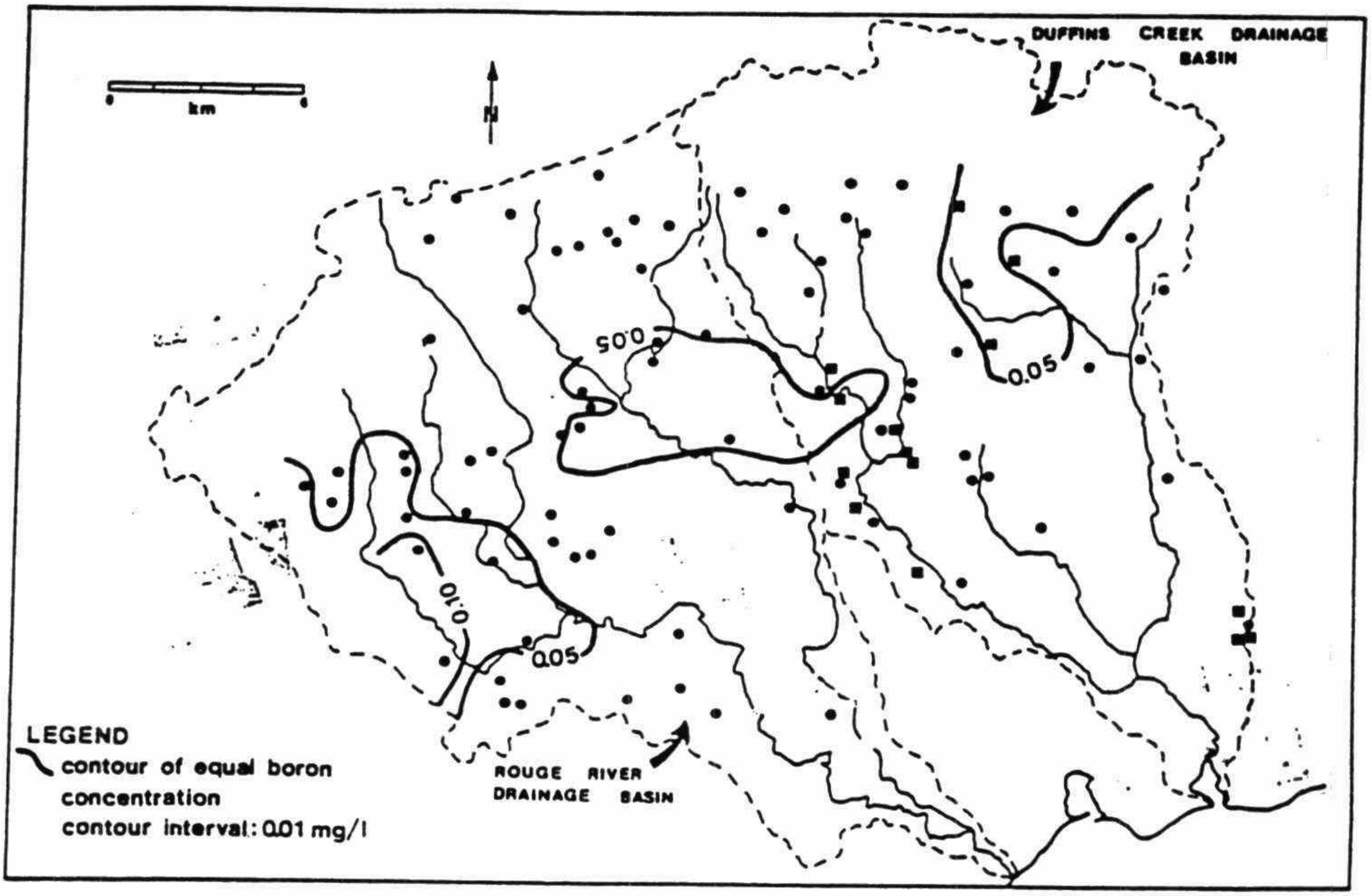
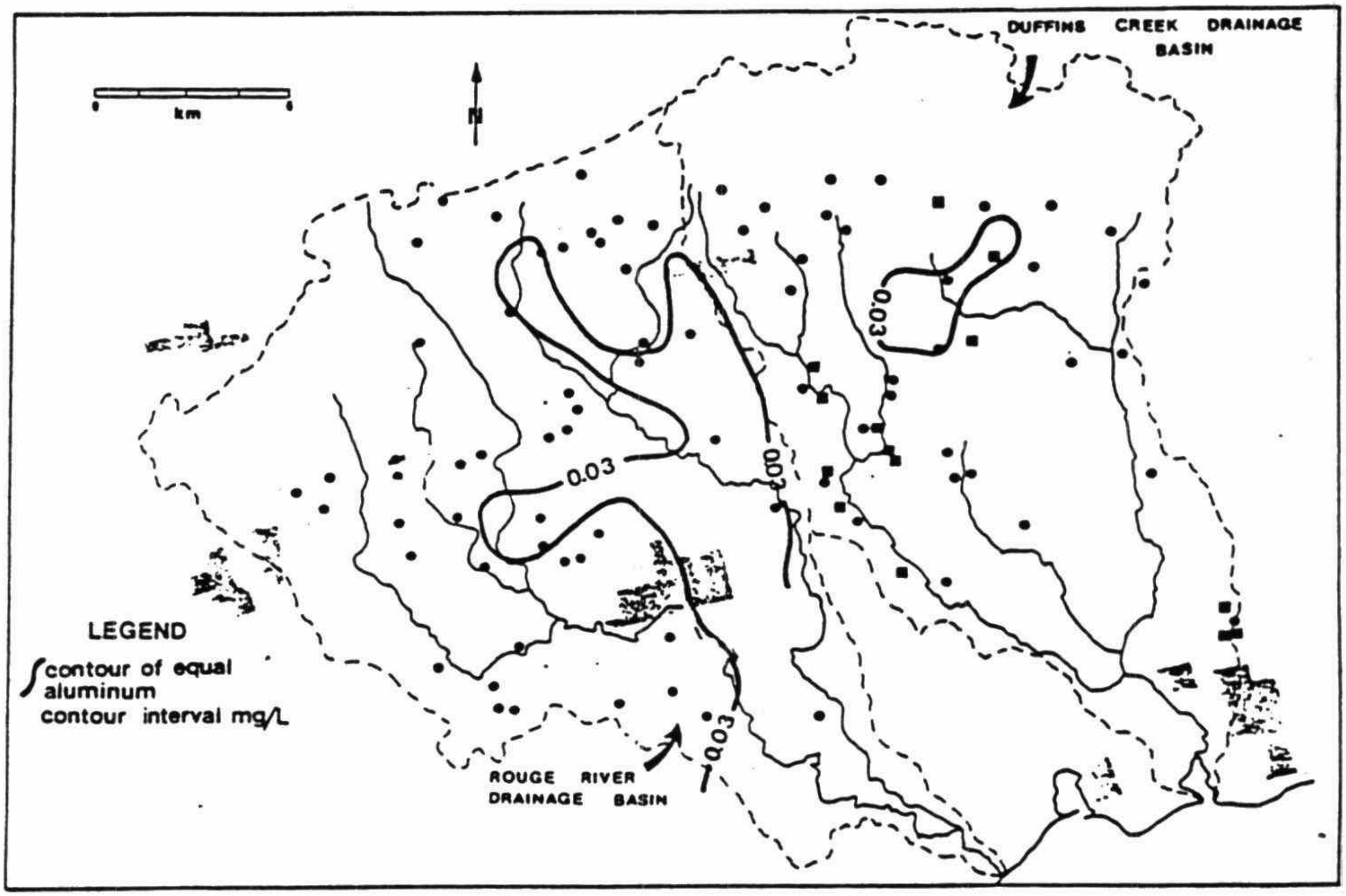

DUFFINS CREEK DRAINAGE BASIN
km
N
0.05
0.05
0.05
0.10
0.05
ROUGE RIVER DRAINAGE BASIN
LEGEND
contour of equal boron concentration
contour interval: 0.01 mg/l

Figure VI-5 Distribution of boron, Duffins Creek-Rouge River basins



DUFFINS CREEK DRAINAGE BASIN
km
N
0.03
0.03
0.03
0.03
0.03
LEGEND
contour of equal aluminum contour interval mg/L
ROUGE RIVER DRAINAGE BASIN

Figure VI-6 Distribution of aluminum, Duffins Creek-Rouge River basins

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Distribution, origins and
behaviour of local groundwaters
containing elevated
concentrations of chlorides /

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